

# MERCURY

## IN THE ATMOSPHERE

A Literature Review

October 1978

TD  
887  
.M37  
M47  
1978  
MOE



Ministry  
of the  
Environment

The Honourable  
Harry C. Parrott, D.D.S.,  
Minister

Graham W. S. Scott,  
Deputy Minister

MERCURY  
IN THE ATMOSPHERE

A Literature Review

Provincial Lottery Trust Fund

Project No. 78-014-13

Interim Report

Prepared For

Air Resources Branch  
Ontario Ministry of the Environment

By  
Ontario Research Foundation

October 1978

### Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at [copyright@ontario.ca](mailto:copyright@ontario.ca)

PROJECT DATA

PROJECT TITLE: A Study of Atmospheric Mercury Deposition in Ontario

REPORTS: (Interim) Mercury in the Atmosphere - A Literature Review

PROPOSAL NUMBER: 5

PROJECT NUMBER: 78-014-13

PRINCIPAL INVESTIGATOR AND AFFILIATION: Ontario Research Foundation,  
Sheridan Park Research Community,  
Mississauga, Ontario. L5K 1B3

LIAISON OFFICER OR SUPERVISOR: S. Gewurtz,  
Air Resources Branch,  
Ontario Ministry of the Environment,  
880 Bay Street, Fourth Floor,  
Toronto, Ontario. M5S 1Z8

RESEARCH

CATEGORY: SOLICITED CONTRACT   X   MULTI-YEAR PROJECT   X  

OBJECTIVE:

Long-range atmospheric transport may make an important contribution to surface deposition of mercury in areas remote from known point sources. The primary objective of this study will be to collect experimental data on atmospheric levels and deposition rates of mercury at specific locations in Ontario. These results will be used to estimate the total deposition flux of mercury to land and water surfaces in urban and rural areas of Ontario, and thus define the relative importance of the atmosphere as a medium for the transport of mercury.

DESCRIPTION:

The study will be initiated with a literature review, with emphasis on atmospheric transport and conversion processes, and sampling and analytical methodology. Suitable techniques for the measurement of airborne concentrations and deposition will be developed. A mobile field monitoring station will be assembled and operated for 6 months in the Toronto and Huntsville areas. Airborne concentrations and deposition rates of mercury, and relevant meteorological parameters required for interpretation of the results will be measured at these sites. Elemental, organic and particulate mercury components will be identified. In subsequent optional phases of the study, a one-year survey involving four sampling sites and an in-depth evaluation of the data may be undertaken.

The proposed programme should provide adequate experimental data to accurately define the total deposition flux of mercury to land and water surfaces in Ontario at the specified sampling sites. The relative importance of various forms of mercury, and the specific scavenging mechanisms which remove mercury from the atmosphere, should also be defined. An effort will be made to define the atmospheric conditions most often associated with high rates of mercury deposition.

DURATION

OF PROJECT:   3   YEARS

FY 78/79 YEAR IS:   1st   YEAR

BUDGET: TOTAL PROJECT = \$298,700

FINAL REPORTING DATE: 1981



# DISCLAIMER

This report was prepared by consultants under contract to the Ontario Ministry of the Environment. The views and findings expressed herein and the quality and accuracy of the text are the sole responsibilities of the contractor. Opinions and recommendations expressed are those of the contractor and should not be construed to represent policy of the Ministry of the Environment or the Government of Ontario. Mention of specific brand or trade names does not constitute an endorsement by the Government of Ontario.

TABLE OF CONTENTS

Page Number

ENTERED AUG 02 2001

SUMMARY	1
1. INTRODUCTION	3
2. THE LITERATURE ON MERCURY IN THE ENVIRONMENT	5
3. SOURCES AND USES	7
4. PREVAILING SPECIES AND AMBIENT LEVELS OF MERCURY IN THE ATMOSPHERE	17
4.1 Mercury Species in the Atmosphere	17
4.2 Global Background Levels	18
4.3 Urban vs Rural Concentrations	19
4.4 Levels in Ontario	22
4.5 Vertical Distribution	22
4.6 Diurnal and Seasonal Patterns	23
4.7 Precipitation	25
4.8 Mercury Concentrations Over Water and Land	26
5. THE SAMPLING AND ANALYSIS OF ATMOSPHERIC MERCURY	33
5.1 Solid Samples	33
5.2 Liquid Samples	34
5.3 Vapour Phase Mercury	36
5.3.1 Liquid Impingement	36
5.3.2 Solid Adsorbents	37
5.4 Instrumental Methods	41
6. ATMOSPHERIC TRANSFORMATION AND TRANSPORT	44
6.1 Atmospheric Transformations	44
6.2 Atmospheric Transport	48
7. CONCLUSIONS	59
8. REFERENCES	64
APPENDIX I AN ANNOTATED BIBLIOGRAPHY ON THE GEO- CHEMISTRY OF MERCURY	79
APPENDIX II CONTRACTOR'S TERMS OF REFERENCE FOR THE STUDY TO DETERMINE ATMOSPHERIC MERCURY DEPOSITION.	93

## LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE NUMBER</u>
1.	Present Day Global Cycle of Mercury	12
2.	Trade and Consumption of Elemental Mercury in Canada in 1970	13
3.	The Altitude Dependence of the Concentration in the Atmosphere of Mercury Vapour	28
4a.	Mercury Concentrations in Air Measured During Meteor Cruise No. 32a Over the North Atlantic	29
4b.	Diurnal Variation of the Hourly Average Mercury Concentration	29
5.	Cycle of Mercury Interconversions in Nature	57
6.	Pre-Man Global Cycle of Mercury	58

## LIST OF TABLES

<u>TABLE</u>		
1.	Mercury Emissions in the United States in 1973	14
2.	Mercury Consumption in the United States, 1970-1973 and Projected for 1985	15
3.	Total Mercury Losses in 1973 for the Coterminous United States	15
4.	1970 Mercury Emissions in Canada	16
5.	Summary of Current Data on Atmospheric Mercury Levels for Various Locations	30
6.	Summary of California Atmospheric Mercury Measurements	31
7.	Regional Variations in Speciation of Atmospheric Mercury in Tampa, Florida	32
8.	Elemental and Total Atmospheric Mercury Concentrations in Three North Carolina Cities	32

## SUMMARY

The cause of elevated mercury levels occurring in the fish of freshwater lakes remote from known sources, in Ontario and elsewhere, has yet to be identified. This review of the literature which considered natural and anthropogenic sources, prevailing ambient concentrations, sampling and analytical methodology, and atmospheric transformation and transport of mercury, was undertaken as the first stage of an experimental study to determine the importance of the atmosphere as a medium for the transport of mercury to land and water surfaces in Ontario.

Mercury in the environment arises from many diverse sources and current estimates suggest that man's activities may account for 5 - 30% of the total emissions. Dispersion studies and deposition measurements in the vicinity of point sources show that a major portion of such emissions are widely dispersed and thus become part of the continental reservoir. A portion of natural emissions to the atmosphere may occur as organomercury compounds arising from biological processes involved in soil and water degassing. Elemental mercury vapour appears to be the principal form in which atmospheric mercury exists and thus the conversion of organomercury compounds to elemental mercury may be an important transformation occurring in the atmosphere. The limited data available indicate that mercury is adsorbed on particulates to only a limited extent ( $\sim 4\%$ ). Although extensive monitoring results are not available, prevailing ambient concentrations have been defined and the lowest levels occur over the oceans and other remote regions. Continental background levels are intermediate to these low levels and the high levels found in the vicinity of known sources.

Sampling and analytical procedures which have been developed for the measurement of airborne mercury concentrations have been assessed. Emphasis has been placed on the analysis of different types of samples (particulate and vapour state mercury compounds in ambient air and precipitation) as well as on those procedures and techniques which are considered of greatest relevance to the development of a continuous atmospheric mercury monitoring programme with limited speciation studies. Precipitation sampling and preservation has received very little attention to date, and while more significant advances have been made in relation to vapour mercury sampling and analysis, information is limited as to the reliability and efficiency of many of the published methods when applied to atmospheric sampling programmes.

Global mercury cycles have been derived in recent years in an attempt to provide a quantitative assessment of the relative importance of natural and anthropogenic sources, and to define the important pathways and sinks for mercury. The atmosphere is shown to be an important transport medium for mercury, with a currently estimated residence time of only 11 days, compared to thousands of years for other compartments of the environment. Little is known about the deposition mechanisms whereby mercury is removed from the atmosphere. The net efficiency of precipitation washout as a deposition mechanism may be less than previously estimated because of recycling between the soil and atmosphere, and dry vapour deposition on fresh water surfaces has been suggested as a possible mechanism to explain the high mercury levels in biota of remote lakes. An involvement of acid rain has been implied by recent studies but no specific mechanisms have been defined.

## 1. INTRODUCTION

Mercury is neither abundantly nor widely distributed in the earth's crust, and ranks 16th from last in the list of abundance of elements in the earth's crust (1). However, the element is found in trace amounts throughout the lithosphere (rocks and soil), the hydrosphere, the atmosphere and the biosphere (2,3,4). Natural processes which have been releasing mercury to the environment for billions of years include the weathering of mercury-containing mineral formations, soil degassing and volcanic emanations, and numerous estimates (5,6,7) of the relative importance of these emissions on global and continental scales have been made. Major anthropogenic sources (8) from which mercury can be emitted into the atmosphere include the combustion of fossil fuels, sulphide ore smelting, cement production, the production of caustic and chlorine in the mercury cell chlor-alkali process, and municipal and other waste incineration of mercury-containing articles such as batteries, lights and switches. Miscellaneous industrial sources also account for a major proportion of the mercury involved in human activities (9,10,10a) because of the unique combination of physical and chemical properties that it provides. These uses in conjunction with the emissions from natural sources make mercury an ubiquitous element which is found throughout the environment. This multitude of sources, both natural and man-made, is one of the more difficult aspects of mercury pollution and many controversial points concerning the relative importance of source types, and details of transport mechanisms and atmospheric transformations have yet to be resolved. The existence of numerous chemical forms and physical states of mercury in the environment is a further complexity that must be recognized.

The environmental concern over mercury which has developed during the past two decades has arisen primarily from the acute toxic effects which have occurred among people eating fish contaminated with high levels of the metal. In Canada, the subject has received attention since the late 1960's, when rivers and lakes in Ontario were closed to fishing because of mercury pollution (7,10). In the early incidences, contamination could generally be traced to some local industrial source, but as the investigations continued, the metal was found to exist in organisms and the environment in general in

significant amounts in areas quite remote from any known sources. Rivers in Northern Ontario and lakes in the Muskoka district of Ontario, the Adirondacks in New York State, and Southeastern New Brunswick are specific North American examples that have been identified (11).

Several theories have been proposed to explain these occurrences of mercury contamination of the food cycle in areas remote from known sources. In the absence of local anthropogenic or natural sources, long-range atmospheric transport is considered a possible mechanism whereby mercury is so widely distributed in the environment (12).

Because of the general lack of quantitative data on prevailing atmospheric levels and deposition rates of mercury in Ontario, no firm conclusions can be made at this time regarding the importance of atmospheric transport in contributing to the mercury content of fish in lakes and rivers remote from urban and industrialized areas. The primary objective of this study (13) is to collect experimental data on atmospheric levels and deposition rates of mercury which will permit an estimate of the total deposition flux to land and water surfaces in specific urban and rural areas of Ontario. This literature review has been conducted as the first phase of the study, with the objective of acquiring all data and information relevant to the experimental studies to be undertaken.

## 2. THE LITERATURE ON MERCURY IN THE ENVIRONMENT

An extensive literature on the environmental aspects of mercury has developed only during the last decade. Several bibliographies (14,15, 16) have been prepared and the very recent increase in concern with mercury in the environment has lead to the preparation of a number of reviews, some of which have been published quite recently. While some of these studies are very general in coverage (2,4,17), others attempt to provide a focus on more specific aspects of the subject. Geological aspects of mercury occurrence in the environment were the focus of several earlier reviews, (18, for example). More recently, both anthropogenic and natural sources have received attention in several documents (10,10a,19,20,21) and production and uses (22) and emissions (8) in Canada have been assessed. Prevailing concentrations in the atmosphere and other segments of the environment have received attention in the most recent reviews (5,6,12) and the continuing difficulties associated with the measurement of ambient mercury concentrations and the mercury content of other environmental samples also are discussed in these same reviews. The occurrence of mercury in food and man and the resulting effects on human health have been discussed in most reviews (2,5,6,9,10,23). Transformation and transport mechanisms have also been the subject of several reviews, despite the rather limited number of specific experimental studies that have been reported (5,12,24,25).

A criteria document has been prepared by at least one state agency (26) and a limited number of publications on legislation pertaining to mercury pollution in Canada (10,21,27) are available.

Subject areas within the general topic of mercury in the environment can be defined as follows:

- analytical and sampling methodology
- sources, both natural and anthropogenic
- prevailing concentrations in the environment
- transport and transformation mechanisms
- ecological effects
- health effects



In this review emphasis has been placed upon the first four subject areas with attention focused upon mercury in the atmosphere. Of particular importance to subsequent phases of the study was the collection of all relevant information on sampling and analytical methodology for the measurement of ambient concentrations and deposition rates of particulate and vapour mercury. A total of approximately 280 references were evaluated in the initial search of the literature and of these 185 were considered sufficiently relevant to the subject of this review to be cited. A reference file on these other less relevant articles has been maintained for future reference.

An annotated bibliography on the inorganic geochemistry of mercury in the natural environment was prepared by J. Robbins, Scintrex Limited, as background material for this review. Selected articles are discussed in the text and the entire bibliography is included for further reference in Appendix I.

### 3. SOURCES AND USES

It is widely recognized that mercury is released from numerous natural and anthropogenic sources. While some of these have been quantitatively defined, it is more difficult to quantitatively assess the relative importance of these two major source classes and this aspect of the mercury problem has received considerable attention in numerous recent reviews (2,4-7,12,28). Because of the quite substantial contribution that can be made by natural sources, it is important that these inputs be understood before attempting to assess the importance of specific man-made sources on atmospheric levels, since their impact may be masked by relatively small changes in larger natural sources. In assessing the relative importance of natural and anthropogenic sources, the lack of detailed data generally has required that long term, large scale comparisons be made to determine the overall impact of man's activities on environmental mercury levels. While this technique has been extremely useful in determining global cycle and transport models, the need to assess shorter term and more localized effects should not be overlooked.

Mercury occurs in trace amounts in the earth's crust and tends to be present near the surface as a cinnebar ore of mercuric sulphide in metamorphic rock formation (10,29,30). It ranks 16th from the bottom of the list in abundance of elements in the earth's crust (1) and is probably present as elemental mercury in the earth's core (30). The release of mercury to the environment by natural processes is due to weathering of mineral deposits, soil degassing, volcanic eruptions, geothermal steam field releases and ore and petroleum deposit volatilization (2,7,30,31). There is also recent evidence that vascular plants can emit significant amounts of mercury (32,33).

During the last decade considerable attention has been given to the quantitative estimate of the relative importance of these natural sources in order to define global mercury cycles and the results have been consolidated and discussed in recent reviews (5,6). Figure 1 summarizes the data considered applicable to present day global cycles for mercury, which will be discussed in further detail in Section 6.2, and a general indication of

the relative importance of the various "natural" emissions to the atmosphere is provided by the following data:

<u>SOURCE</u>	<u>RATE (g/yr)</u>	<u>%</u>
Continental Degassing	$178 \times 10^8$	66.2
Oceanic Emissions	$76 \times 10^8$	28.3
Coastal Ocean Emissions	$14.2 \times 10^8$	5.2
Organic Vapours and Particles from land biota	$0.4 \times 10^8$	0.2
Volcanic Emissions	$0.2 \times 10^8$	0.1
	<hr/>	<hr/>
TOTAL	$269 \times 10^8$	100
Anthropogenic Emissions	$100 \times 10^8$	-

Thus continental degassing accounts for a major proportion of the total natural emissions. Specific processes in this category include weathering of mineral deposits, soil degassing, ore and petroleum volatilization and geothermal activity. Earlier studies indicated that soil degassing accounted for 80 - 96% (34) and 50% (35) of the total mercury released by all sources, and so it would appear that soil degassing is the predominant natural source of mercury emissions to the atmosphere. The figures quoted above suggest that emissions by plants and volcanoes (36,37) are relatively unimportant on a continental or global scale.

Total anthropogenic emissions to the atmosphere are estimated at  $100 \times 10^8$  g/yr (Figure 1) and so account for approximately 27% of total emissions from all sources. Using mercury degassing rates measured by McCarthy et al (4), Van Horn (20) conducted a state-by-state inventory of mineralized and non-mineralized areas and the results are listed in Table 1. The amount contributed by man to air ranged from a low of 2% in Wyoming to a high of 90% in Rhode Island, indicating the large degree to which local variations can occur. However, these variations in man-made contributions must be interpreted with care because each state has a different natural degassing rate. Thus, states with a low natural rate will show a relatively large contribution by man, even though these anthropogenic emissions could

be much lower than those in a state with high emission rates from both sources (6).

Because of its many desirable, and unique, physical and chemical properties, mercury is used by man in a large number of diverse applications, and an equally diverse set of opportunities for loss to the environment exists. Van Horn (20) prepared a detailed summary of past, present and future mercury consumption patterns in the United States and the results are summarized in Table 2. Electrical apparatus, followed by caustic/chlorine production, were the two largest uses and in projections for 1985, caustic/chlorine production continues as the second highest use, although at somewhat reduced levels. In Canada, an evaluation of 1970 data (8) showed chlor-alkali use as the largest item (Figure 2) but improved control methods are now used and it has recently been reported by Environment Canada that current (1978) losses from chlor-alkali plants have been reduced to 1% of 1970 levels (38).

The many uses of mercury have been discussed quite extensively in earlier reviews (5,6,10,19,21,22) and therefore will be summarized only briefly in this report since a detailed assessment of anthropogenic sources is not within the scope of this study. Agricultural uses involve the use of organomercurials as fungicides through application as seed dressing. A decline in this use is anticipated. Mercury is used to prepare various catalytic salts which are used in a number of chemical processes. Dental preparations are an amalgam composed of silver, tin, copper and sometimes zinc, mixed with mercury to form a plastic mass which can be molded into tooth cavities. The production of mercury batteries and alkaline energy cells is the largest single use in the electrical apparatus category. Other uses include mercury pool rectifiers and power tubes, a variety of lamps and switches. The chlor-alkali industry produces chlorine and sodium hydroxide and the use of mercury cells became very prevalent because of the higher purity caustic soda produced. Unfortunately, these cells lost considerable amounts of mercury to the environment. In Sarnia, Ontario, for example, as much as 200 lb/day were being lost (19) but improved control techniques are now used and, as mentioned above, current losses from this industry in Canada are equal to 1% of 1970 levels. Organo-

mercurials are widely used as bactericide and fungicide agents to protect water based paints from bacterial fermentation and a similar application has been made in the pulp and paper industry. Mercury is also lost from laboratories in universities, hospitals and industry, and such losses presumably enter the environment through sewage facilities.

Other anthropogenic activities resulting in the emission of mercury to the environment are fossil fuel combustion (39-45), ore smelting and refining, incineration and sewage treatment. Total mercury losses in 1973 for the United States from anthropogenic sources are given in Table 3 and it can be seen that commercial, industrial and consumer consumption account for a major portion of the total emissions. The relatively small contribution by mining and smelting activities is worth noting. Emissions due to energy production (coal, oil, gas combustion) have a proportionately greater impact on the atmosphere than do other categories and this is a consequence of the well established fact that at least 90% of the mercury content of fuels is emitted as a vapour in stack gas.

The production and use of mercury in Canada has been documented by Bangay (22) and anthropogenic emissions have been estimated to be 82.2 tons in 1970 (8). The breakdown by source type is given in Table 4 and the large contribution being made by the chlor-alkali industry at that time is apparent. This supposedly has been reduced to approximately 0.26 tons/year by improved control techniques (38). The diversity of sources is clearly demonstrated by the fact that the miscellaneous category accounts for 51% of all emissions. The relatively large contribution from petroleum combustion compared with coal should be noted. Data for the U.S. (20) show the reverse pattern, with emissions from coal being approximately four times those for petroleum, and this presumably reflects a greater dependence on coal as a fuel in the U.S. than in Canada. Sherbin (21) has discussed anthropogenic sources of mercury in considerable detail, including information on Canadian sources. Particular attention is given to chlor-alkali plants and the closing down of mercury cells in Ontario during the 1973-75 period. Other source categories discussed include: mining and smelting, sewage treatment plants, pulp and paper mills, agriculture and

amalgamation processes.

Existing regulations and legislation at both the provincial and federal level governing mercury emissions to the Canadian environment have been summarized and assessed in recent reviews prepared by the Science Council of Canada (10) and Environment Canada (21). The Science Council study provides an excellent summary of actions taken and lists some legislative and regulatory actions required to prevent further mercury contamination of the environment. Sherbin (21) has listed and briefly discussed the specific Acts, Standards and Regulations pertaining to the control of mercury use and emissions in Canada.

This brief review of sources of mercury, both natural and anthropogenic, shows the many complexities that exist with respect to quantitatively defining mercury emissions to the environment. Natural sources are believed to account for approximately 2/3 of all emissions to the atmosphere, making it very difficult to clearly establish cause and effect relationships when mercury contamination occurs in a specific area or sector of the environment.

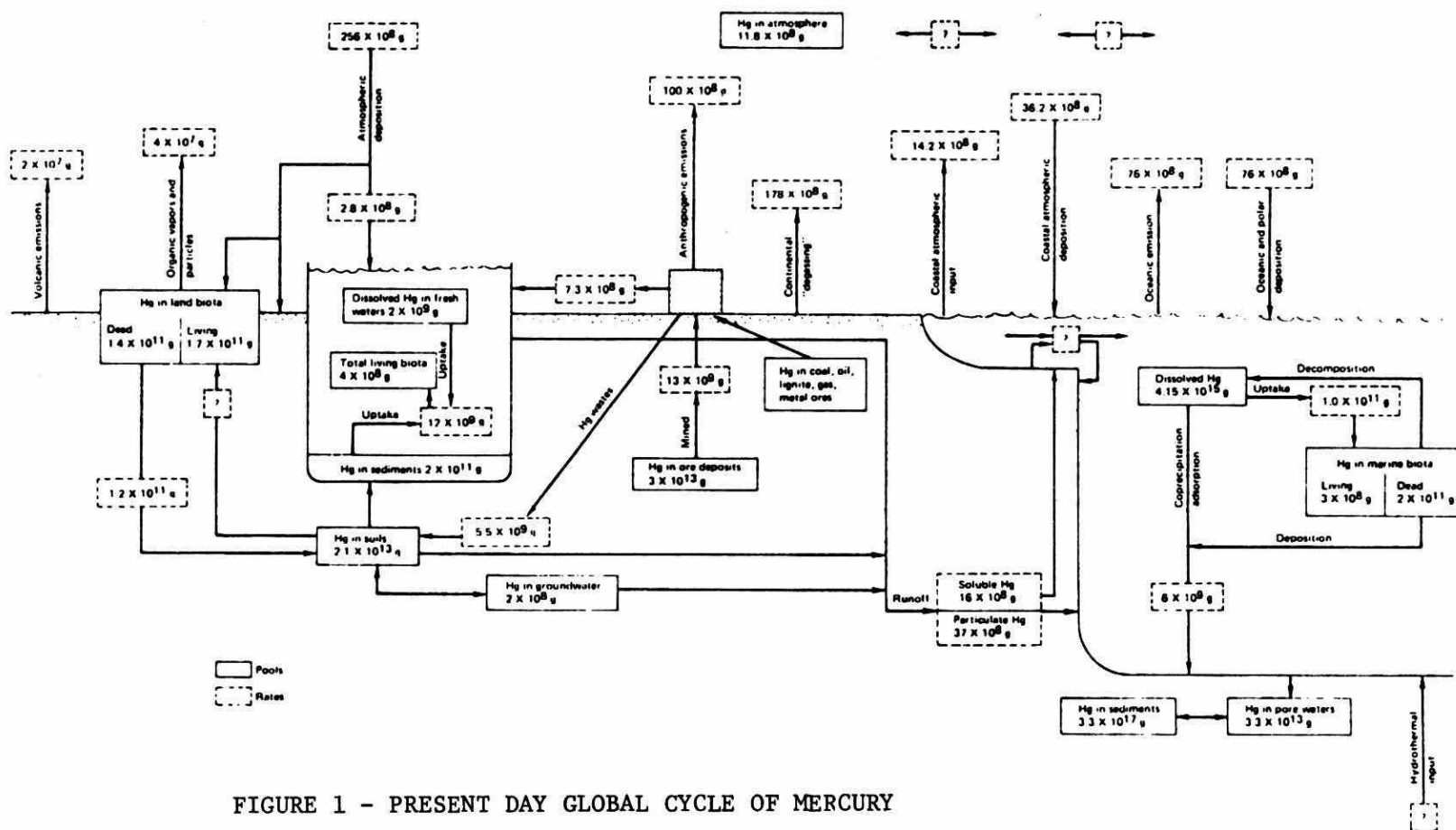


FIGURE 1 - PRESENT DAY GLOBAL CYCLE OF MERCURY

From reference (6)

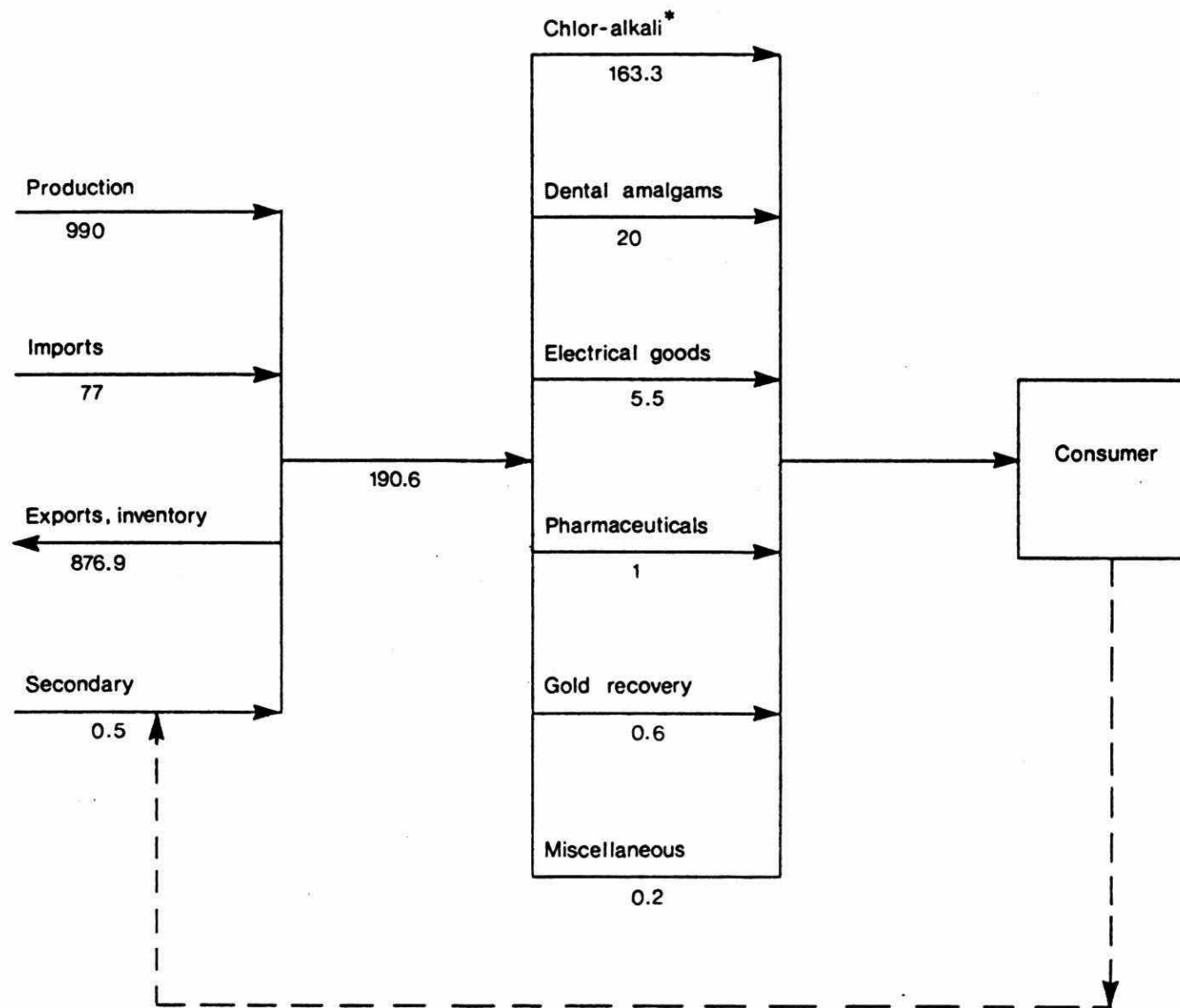


FIGURE 2 - TRADE AND CONSUMPTION OF ELEMENTAL MERCURY IN CANADA IN 1970 (tons)

From reference (3)

\* includes mercury usage for operational requirements, new equipment and installations and stockpiles



TABLE 1. Mercury Emissions in the United States, 1973

	Man-made Losses to		Natural Losses to		Percent Due to Man	
	Air	Water	Air	Water	Air	Water
			(10 <sup>6</sup> g/yr)			
Alabama	9.9	2.5	9.6	4.1	51	38
Arizona	22.3	2.4	85.8	11.3	21	18
Arkansas	3.0	1.8	9.8	2.0	23	47
California	36.8	14.2	118.2	26.3	24	35
Colorado	3.5	1.6	39.2	6.0	8	21
Connecticut	6.0	2.0	1.8	0.01	77	99
Delaware	1.9	0.5	0.4	0.01	83	98
Florida	12.1	4.6	10.2	0.8	54	85
Georgia	9.5	3.2	22.0	2.7	30	54
Idaho	2.8	0.6	31.3	6.3	8	9
Illinois	22.4	8.0	10.5	1.4	68	85
Indiana	12.2	3.8	6.8	3.2	72	54
Iowa	5.6	2.0	10.6	5.9	35	25
Kansas	3.7	2.1	15.5	2.2	19	49
Kentucky	10.5	2.1	7.5	1.2	58	64
Louisiana	8.4	2.6	8.5	0.5	50	84
Maine	2.5	0.7	5.8	0.3	30	70
Maryland	7.6	3.0	3.7	0.1	67	97
Massachusetts	11.4	3.9	3.0	0.6	79	87
Michigan	18.8	5.2	10.7	0.8	64	87
Minnesota	7.0	2.7	14.9	6.0	32	31
Mississippi	5.1	1.4	8.9	4.3	34	25
Missouri	13.8	3.4	13.0	4.6	50	43
Montana	4.0	1.0	55.0	1.9	7	34
Nebraska	2.3	0.7	14.5	1.9	14	27
Nevada	5.6	0.3	83.1	4.2	6	7
New Hampshire	1.4	0.3	3.4	0.1	29	75
New Jersey	14.6	3.4	1.4	0.2	91	94
New Mexico	4.9	0.5	45.9	20.7	10	2
New York	35.5	7.1	18.1	0.6	66	92
North Carolina	12.2	2.2	18.5	1.2	40	65
North Dakota	0.9	1.0	13.1	0.9	6	53
Ohio	25.3	4.5	7.8	1.8	76	71
Oklahoma	4.6	1.3	13.0	25.5	26	5
Oregon	3.6	0.8	72.7	2.6	5	24
Pennsylvania	34.8	5.1	17.0	0.8	67	86
Rhode Island	1.8	0.4	0.2	0.02	90	95
South Carolina	5.5	1.2	5.7	1.1	50	52
South Dakota	1.1	0.4	14.4	1.3	7	24
Tennessee	10.0	2.3	7.8	5.2	56	31
Texas	25.9	4.7	49.6	18.5	34	20
Utah	7.8	0.7	31.0	3.0	20	19
Vermont	0.7	0.2	2.2	0.2	24	50
Virginia	8.1	1.8	15.0	1.1	35	62
Washington	9.0	1.5	25.2	0.9	26	63
West Virginia	5.4	0.8	9.1	0.6	37	57
Wisconsin	8.4	2.3	10.3	0.9	45	72
Wyoming	0.7	0.1	36.8	2.9	2	3

From reference (6)

**TABLE 2 Mercury Consumption in the United States, 1970-1973 and Projected for 1985**

End Use Activity	1970	1971	1972	1973	Projected for 1985
	(10 <sup>6</sup> g)				
Agriculture	62.3	50.8	63.2	62.9	24.1
Catalysts	77.0	34.3	27.5	23.2	17.2
Dental preparations	78.6	64.4	102.6	92.2	129.0
Electrical apparatus	548.7	572.6	535.0	619.2	662.0
Caustic chlorine	516.4	421.5	396.2	449.6	481.6
Laboratories	62.1	46.7	20.4	22.6	?
Industrial instruments	166.2	134.4	225.0	246.1	447.2
Paints	355.9	296.0	282.8	261.5	106.6
Pharmaceuticals	23.7	23.0	19.9	20.8	17.2
Other	209.3	170.0	147.2	69.1	206.4
<b>TOTAL (rounded)</b>	<b>2100</b>	<b>1814</b>	<b>1820</b>	<b>1867</b>	<b>2091</b>

From reference (6)

**TABLE 3 Total Mercury Losses in 1973 for the Coterminous United States**

Activity Description	Total Losses to			Total Hg Lost	Total Hg Recycled
	Air	Water	Land		
	(10 <sup>6</sup> g)				
Hg mining, smelting and processing	7.85	0	0.42	8.27	0
Other mining activities	50.71	3.07	4.91	58.09	0
Energy related activities	104.5	2.18	42.07	148.73	0
Manufacturing and processing (see Table 1.3)	26	21.72	271.33	319.05	20.66
Commercial, industrial and consumer consumption	282.2	60.73	646	990	126.11
TOTAL	471.26	87.70	964.73	1524.73	146.77
Sewage	4.01	19.92	22.88	46.0	
Natural degassing	1018.7			1018.7	

From reference (6)

TABLE 4 1970 MERCURY EMISSIONS IN CANADA

Source	Emissions	
	Tons	Percent
<b>PRODUCTION</b>		
Mercury mining	1.05	1.3
Mercury beneficiation	0.76	0.9
Secondary production	0.004	*
Distillation	<u>0.002</u>	<u>*</u>
Production total	1.82	2.2
<b>METALLIC MERCURY USE</b>		
Chlor-alkali industry	26.4	32.1
Dental amalgams	0.17	0.2
Electrical equipment	0.003	*
Gold recovery	0.28	0.3
Pharmaceutical manufacture	0.0001	*
Instrumentation	<u>0.03</u>	<u>*</u>
Mercury use total	26.88	32.7
<b>MERCURY COMPOUND USE</b>		
Agriculture	1.5	1.8
Paint manufacture	0.036	*
Battery cathodes	0.008	*
Pharmaceutical use	<u>0.65</u>	<u>0.8</u>
Mercury compound use total	2.20	2.7
<b>MISCELLANEOUS</b>		
Paint use		
Interior	0.99	1.2
Exterior	5.04	6.1
Coal combustion	6.99	8.5
Petroleum combustion	20.0	24.3
Natural gas combustion	0.002	*
Wood combustion	2.87	3.5
Refuse incineration	4.44	5.4
Sewage sludge incineration	0.54	0.7
Fluorescent tubes	0.94	1.1
Thermometer breakage	0.4	0.5
Zinc recovery	5.26	6.4
Copper recovery	3.42	4.2
Lead recovery	<u>0.40</u>	<u>0.5</u>
Miscellaneous total	51.29	62.4
<b>TOTAL</b>	<b>82.19</b>	<b>100.0</b>

\* Negligible (less than 0.1%).

From reference (8)

#### 4. PREVAILING SPECIES AND AMBIENT LEVELS OF MERCURY IN THE ATMOSPHERE

##### 4.1 Mercury Species in the Atmosphere

The fundamental chemistry and geochemistry of mercury and its compounds has been discussed in earlier reviews (2,3,4,18). As summarized in the previous section, emissions from anthropogenic sources are predominantly in the elemental form, whereas natural sources involving biological processes are thought to give rise to organomercury compounds. Because of the many reactions that mercury can undergo, the atmospheric chemistry of mercury is extremely complex and involves numerous compounds which may exist in the form of vapours, particulates, or adsorbed species on other particulate matter.

Three oxidation states are possible for mercury and the current literature (5,12,46) indicates that the principal compounds occurring in the atmosphere are:

- elemental mercury vapour ( $\text{Hg}^0$ )
- mercury (II) chloride vapour ( $\text{HgCl}_2$ ), and possibly other volatile salts
- various species adsorbed on particulate matter
- methyl mercury (II) compounds ( $\text{CH}_3\text{-Hg.Cl}$  for example) and dimethyl mercury [ $(\text{CH}_3)_2\text{Hg}$ ].

The rate of vaporization of mercury and certain of its inorganic compounds decreases in the sequence  $\text{Hg} > \text{Hg}_2\text{Cl}_2 > \text{HgCl}_2 > \text{HgS} > \text{HgO}$  (47), and the more toxic organomercury compounds also are quite volatile. Despite the fact that this variety of mercury compounds can exist as vapours in the atmosphere, elemental mercury is found to be the principal gaseous constituent in most studies (5,12,46). Salts and oxides could be expected to be the principal mercury compounds found as an integral component of atmospheric particulate matter, and in earlier work (48,49) it was assumed that elemental mercury adsorbed strongly on most particulates. The situation is less well defined for organomercury compounds but it would appear reasonable to assume a similar, and perhaps even greater tendency to adsorb on fine particulate materials. This is an area in need of further

study.

In earlier environmental studies, methodology was not developed to an extent that enabled identification of various forms of mercury, and elemental mercury vapour or particulate mercury were the only forms measured. More recently, techniques have been developed to measure total mercury and also to separate various compound groups or mercury species. The results of the more recent studies where mercury has been measured in various locations will be discussed in the following sections.

#### 4.2 Global Background Levels

Airborne mercury concentrations depend on the geographical location, meteorological conditions, altitude, season of the year and time of day. From global balances, the present estimate of total annual flux of mercury to the atmosphere is from 41,000 to 50,000 metric tons per year (6). The estimated atmospheric content of mercury is in the order of 1200 metric tons and this is a negligible amount in comparison to the content of the ocean and earth crust.

Mercury vapour concentrations in the air may vary from less than  $1 \text{ ng.m}^{-3}$  in remote areas to tens of thousands of  $\text{ng.m}^{-3}$  near ore deposits (50) and in areas of volcanic activity (37). The estimated world wide average atmospheric concentration has been previously estimated at  $20 \text{ ng.m}^{-3}$  (23), but this value probably is high, as implied by the more recently measured data used to calculate global mercury balances. A recent model (6) used surface altitude levels of  $0.7 \text{ ng.m}^{-3}$  for oceanic and polar air,  $1.5 \text{ ng.m}^{-3}$  for oceanic shelf areas and  $4.0 \text{ ng.m}^{-3}$  for continental air, while another used  $2 \text{ ng.m}^{-3}$  as a world average (25). The range of mercury concentrations usually cited for unpolluted air is  $1\text{--}10 \text{ ng.m}^{-3}$  (23,51). The lowest reported average values are  $0.6$  to  $0.7 \text{ ng.m}^{-3}$  of mercury vapour from samples collected at a height of 10,000 ft. over the ocean near San Francisco (48) in agreement with those measured over the USSR at the same height (52). Another series of measurements over the North Atlantic Ocean at sea level resulted in an average concentration of  $3.8 \text{ ng.m}^{-3}$  with a range of  $0.9$  to  $11 \text{ ng.m}^{-3}$  (53). Similarly, a mean of  $2.5 \text{ ng.m}^{-3}$  (all elemental mercury) was found on an unpopulated island in the Baltic Sea (54).

#### 4.3 Urban vs Rural Concentrations

Concentrations of particulate and mercury vapour in remote and rural areas were compared with urban and industrial areas (6) on a world wide basis and are shown in Table 5. While particulate levels were more than an order of magnitude higher in urban than in rural areas, vapour levels were higher by less than a factor of two. Measurements over a two month period in three sparsely populated locations in southeastern Norway showed average mercury vapour levels of  $2 - 4 \text{ ng.m}^{-3}$  (range  $< 0.5 - 14.5 \text{ ng.m}^{-3}$ ) (85), and were considered low in comparison to results from similar measurements at other background locations. In over 3 1/2 months of surveys in the U.S. covering  $30,000 \text{ Km}^2$ , continuous measurements of ambient mercury vapour levels ranged from  $0 - 15 \text{ ng.m}^{-3}$ , but showed no significant distribution pattern (55). Urban measurements of mercury (usually in the form of elemental mercury based on amalgamation sampling techniques) are quite variable, but over 90% of the measurements in U.S. cities were within a range of  $2-60 \text{ ng.m}^{-3}$  with some notable exceptions of very high concentrations near known emission sources (5).

A portion of the total mercury in air is associated with particulates. An average of  $0.03 \text{ ng.m}^{-3}$  particulate mercury measured at an elevation of 3752 m at a remote site in Switzerland compared favourably to other remote locations (56) and contrasts with urban levels in particulates of about  $0.2 - 30 \text{ ng.m}^{-3}$  (57, 64). An extensive monitoring programme for heavy metals, measured simultaneously in various media (air water, sewer, soil and sediments) in the Washington, DC area has shown that most of the mercury in urban air is elemental rather than particulate (58). This is in agreement with other studies in which particulate mercury accounts for roughly 5 to 10% of the total mercury (6,53). For this reason the mercury content of suspended particulates is not measured on a routine basis in the U.S. national air quality survey (5), and further justification for this policy is given by the recent results of Liroy et al (59), which suggests that most metal levels have been decreasing in U.S. cities during the past 5 - 10 years.

Of the mercury associated with particulates, various forms may be

surface bound by condensation or adsorption (e.g., mercury attached to fly ash (60), a component of the particulate itself (e.g. chloride salts, sulphides or oxides of mercury), or complexed with other metals. Preferential attachment of volatilized metals to smaller surfaces with large surface areas may be expected (61). From size distribution measurements of mercury in city air (62), it was concluded that about one half of the mercury was associated with aerosols that passed through the 1.1  $\mu\text{m}$  stage of an Andersen sampler. Unfortunately, most of the levels measured in this and other studies (63) were below the detection limit of the multielement analytical method and therefore the results are of dubious value. Mercury levels in particulates for various cities in Europe (56,63,64) and the United States (57,62,67) ranged from about  $0.2 \text{ ng.m}^{-3}$  to  $30 \text{ ng.m}^{-3}$ . Urban sites showed double the amounts of mercury found at suburban sites within the same city (57). In Rotterdam, summer mean concentrations of particulate mercury were slightly higher than winter concentrations (64). Mercury in airborne particulates are usually observed to be enriched when compared to its natural abundance in the earth's crust (60,62,64,66,68).

When measured near point sources, mercury associated with aerosols was found to increase downwind of coal-fired power plants and contributed to higher levels in both moss (65) and snow (66) near five Swedish chlor-alkali plants. From measurements near coal-fired steam plants it was computed that dry deposition was a more important soil enrichment mechanism than wet deposition, with deposition rates of  $0.04$  and  $0.17 \text{ g.ha}^{-1}$  respectively (66).

Very few long term mercury-in-air monitoring programmes have been conducted and most have measured particulate mercury only. Many forms of mercury have been found in urban atmospheres but man-made sources involving high temperature processes (e.g. fossil fuel burning) are known to emit elemental mercury vapour rather than alkyl forms. Relatively high concentrations have been measured near various types of urban sources and are shown in Table 6. (44,70). Sewage treatment plants have been identified as an anthropogenic source of organomercury, and this is consistent with the recognized role of natural biological processes as

a source of organomercury (46,71).

The largest amounts of airborne organomercury have been measured downwind of sewage treatment plants in various cities in the U.S. and the total mercury vapour concentrations varied from 0.13 (during snowfall) to 60,000  $\text{ng.m}^{-3}$ , with a single measurement of 600,000  $\text{ng.m}^{-3}$  (71). Considerable variation, both in proportion and magnitude, occurred between inorganic mercury, alkyl mercury, elemental mercury and dialkyl compounds. The author's conclusions that elemental mercury concentrations decreased while volatile alkyl forms of mercury increased with increasing distance from the treatment plant were subsequently questioned (72). The study, however, is one of the few that has shown the occurrence of organic and inorganic mercury species in air, apart from the original technique development work (46,73). During development of the technique, measurements at different locations covered a concentration range of 2 to 300  $\text{ng.m}^{-3}$  of total mercury in Tampa, Florida, and are shown in Table 7, with the relative proportion of the individual species identified. From these results it was concluded that a variable distribution of volatile mercury species appear to be given off by water and land surfaces and include: mercury (II) type compounds, methylmercury (II) type compounds, elemental mercury and very little dimethylmercury (73).

In other measurements in three U.S. cities as quoted in a previous review (5), lower organomercury amounts were calculated from the relative concentrations of elemental and total mercury. These results, are shown in Table 8 and reflect that most of the mercury in these cities was in the elemental form.

Speciation measurements based on another technique of mercury compound separation (54) were briefly carried out on a remote island in the Baltic Sea just off the coast of Sweden (74). Lower levels resulted (1.7 - 2.6  $\text{ng.m}^{-3}$ ) and only elemental mercury was found.

It is apparent from the above that mercury monitoring programmes should include the measurement of this organomercury fraction, in view of the large variations that can occur in the ratio of organo and elemental



mercury in the atmosphere.

#### 4.4 Levels in Ontario

A spectrophotometric instrument mounted in a mobile van has been used to measure point of impingement mercury levels in the vicinity of expected emission sources in Toronto, Sarnia, Cornwall and Dryden (75). Background levels were generally found to be less than  $20 \text{ ng.m}^{-3}$ . In the vicinity of one emission source in Toronto, 1/2 hour average levels at the point of impingement were  $2250\text{--}2900 \text{ ng.m}^{-3}$ . More recent sampling, using similar methods, at Balmerton, Cornwall, Dryden and Marathon has indicated mean levels in the range of  $265 \text{ to } 1800 \text{ ng.m}^{-3}$  except for an average concentration of less than  $10 \text{ ng.m}^{-3}$  at an airport (21). Comparable levels were measured with an amalgamation method near four chlor-alkali plants in Quebec and New Brunswick, with overall average concentrations ranging from 110 to  $2500 \text{ ng.m}^{-3}$  (76).

It is apparent from the literature that very limited sampling has been conducted on a long-term basis in areas remote from suspected sources in Ontario and Quebec. Thus it is not possible to confirm that background or urban levels are generally similar to those reported elsewhere. Since mercury concentrations are known to be elevated near mineralized areas (4, 77) of the type that occur to some extent in Ontario (21,78,79,80), there is the possibility that ore body volatilization could contribute to atmospheric mercury levels in remote parts of Ontario, resulting in levels somewhat higher than the typical background levels discussed above.

#### 4.5 Vertical Distribution

The concentration of mercury in air is known to be a function of altitude. Soil air sampled from one meter deep holes was found to contain enriched amounts of mercury, compared to air measured one meter above the ground (3,4). Atmospheric gradients were also measured over mineralized areas from an aircraft and the ground level concentrations were greater than the levels found at 400 ft. by factors of 2 to 200 (4).

An average concentration of  $3.8 \text{ ng.m}^{-3}$  (range  $1 - 11 \text{ ng.m}^{-3}$ ) was

measured from a ship in the north Atlantic (53) but the levels in the troposphere measured from an aircraft (8.5 to 12 km altitudes) were about three times lower and averaged  $1.4 \text{ ng.m}^{-3}$  (range  $0.6 - 2.7 \text{ ng.m}^{-3}$ ). Vertical gradients measured close to the soil surface (0-10 m) generally showed higher levels at 0.1 m than at 10 m from the ground (73). The average concentrations obtained were:  $4.9 \text{ ng.m}^{-3}$  at 0.1 m,  $3.6 \text{ ng.m}^{-3}$  at 1 m,  $3.2 \text{ ng.m}^{-3}$  at 5 m and  $2.7 \text{ ng.m}^{-3}$  at 10 m. Measurements of mercury vapour from 50 - 4000 m altitudes over remote areas in the USSR (52), and up to 200 m on the Swedish coastline (81), confirm earlier measurements and substantiate the altitude dependence of mercury, in that mercury was found to decrease exponentially with height over a concentration range of 7 to  $0.1 \text{ ng.m}^{-3}$  (see Figure 3). These measurements were used to model global cycles (52) and suggest that total amounts in the atmospheric mercury pool are considerably lower than earlier estimates made without consideration of vertical gradients (6).

#### 4.6 Diurnal and Seasonal Patterns

Contradictory evidence on the existence of diurnal patterns for total mercury has been reported (4,12,73). The earlier studies (4) showed that observed mid-day maximum concentrations resulted from mercury release from the soil as a result of the earth's "breathing process". Temperature showed a less obvious effect. Johnson and Braman (73), on the other hand, observed that mercury tended to accumulate at night under stable inversion conditions. Obviously, different mechanisms can prevail depending upon local geological and meteorological conditions. Total mercury was found to be consistently higher during the night than in the daytime in this Florida study (73). This also held true for elemental mercury when measured at 1 m above the ground in a suburban atmosphere. At the particular location, the lowest concentrations roughly corresponded to periods between noon and 18:00 hours which was directly opposed to the air temperature fluctuations. To confirm these results, sampling was repeated at different heights and tended to show a similar pattern.

In San Francisco higher elemental mercury concentrations occurred suddenly in the morning shortly after sunrise on clear days (levels some-

times increased by a factor of four) but the extent of change was minimized on cloudy or foggy days (48). Release from vegetation was postulated. Generally, a decline in concentration was observed in the afternoon, presumably due to changes in the prevailing westerly winds.

Mercury vapour, sampled by silver amalgamation for a two week period over the north Atlantic Ocean was observed to consistently follow a diurnal cycle (53). Maximum concentrations occurred at noon and minimum concentrations during night and early morning, as shown in Figure 4. These variations were particularly apparent on days with strong sunlight, and the concentrations ranged from  $1-2 \text{ ng.m}^{-3}$  at night to  $10-12 \text{ ng.m}^{-3}$  during the day. The magnitude of change was reduced on cloudy or rainy days. Meteorological conditions were not available in the report to permit detailed interpretation of the results; however, a combination of factors which may explain these diurnal variations were suggested as follows: (a) microbially induced organo or elemental mercury releases from the water surface with increased production during daylight hours, (b) mixing of mercury depleted air from the middle troposphere during nocturnal inversions. Another possible explanation may be that daylight conversion of organic mercury or mercury salts thought to be emitted from the ocean (81) to elemental mercury would result in greater collection efficiencies by silver. That is, total mercury may or may not exhibit similar diurnal variations.

Recent measurements have confirmed previous studies that plants release organomercury into the surrounding air from their leaves when either their roots or leaves have been exposed to mercury (32,33). As these studies have shown that little mercury is released by plants at night, higher levels on land may also be anticipated during daylight.

The release of elemental and organic mercury to the atmosphere by volatilization from the ground or water as a function of temperature and time of day has been discussed above and elsewhere (28). Seasonal temperature variations have been shown to influence the atmospheric mercury concentrations (4) and lower values ( $1-25 \text{ ng.m}^{-3}$ ) have been measured in cool wet weather, compared to the higher levels ( $2-50 \text{ ng.m}^{-3}$ )

which were observed under prolonged, warm and dry conditions (48). A seasonal relationship was concluded when lower mercury concentrations in air over the Swedish coastline correlated strongly with lower surface water temperatures (81).

#### 4.7 Precipitation

Measurements of mercury levels in rain water and snow are generally regarded as being difficult from both an analytical and sampling standpoint (12), a fact which may be reflected in some apparently anomalous values in the literature. The chemical forms of mercury in precipitation are not known (6). Levels in Canada range from 0.1 to 0.3 ppb in rain water and 0.01 to 1.33 ppb in snow (21). For snow, the average levels measured in Ontario (0.02 ppb) (82) are a factor of ten lower than the average levels in Quebec, the Atlantic Provinces (21) and the United States (66). Elevated levels of about 2.0 ppb in snow have been observed near chlor-alkali plants but decrease to 0.2 ppb at further distances (83).

Rainfall concentrations in Hakodate, Japan were found to remain constant at 0.001 ppb (a factor of 100 lower than other studies) regardless of the season, the wind direction and amount of rainfall (84). Similar findings and concentrations were observed for snow but mercury vapour concentrations were shown to increase from an urban influence.

Considerable discrepancy exists as to whether rain or snow washes out mercury vapours. Some studies have shown considerably decreased mercury vapour levels following a rainstorm (4). In other studies little change has been observed before, during and after a thunderstorm (73) and maximum ambient mercury concentrations were detected during periods of maximum rainfall rate (86). From measurements of atmospheric gases trapped in soil, it was found that rain very readily washed mercury from the air and that it could take several days before mercury levels return to their former equilibrium levels (31). It is apparent that many local influences demand attention during sampling to enable meaningful interpretation of measured concentrations of mercury in precipitation. Acidification of unbuffered lakes by washout of sulphur dioxide, sulphur trioxide and oxidation products in precipitation has been studied

extensively (61,87,88,89). In northeastern North America, the pH of precipitation is typically between 3.0 and 5.0 (87). Simultaneous measurements of mercury and pH of rain or snow have been done in north-west Quebec (11). Since the mercury content in precipitation was higher than the surrounding waterways by a factor of about ten, precipitation was considered to be a major contributing pathway to elevated mercury levels in lakes. Evidence for mercury dissolution in the collected rainfall was apparent, since the concentration of mercury in the precipitation at the beginning of the rainfall was fifty times higher than at the end (0.5 - 0.01 ppb). The pH was 4.5. Snow core samples, taken above remote ice covered lakes, indicated levels of 0.1 to 0.17 ppb mercury and methyl mercury made up about 1 to 3% of the total mercury, which was near the detection limit of the methods used.

The solubility of mercury vapour in water is 0.2 - 0.3 mg/l at 20°C and is higher than some of its salts (5) and increased solubility is expected with increased acidity (49). Therefore, acid precipitation could prove to be a very effective washout medium for ambient mercury and some possible mechanisms for this are suggested later (Section 6.2). It should also be noted that theoretical gas-liquid equilibrium relationships have been used to show that methyl mercury salts would be four times more soluble in acidified water (pH = 4) than in neutral water (81).

#### 4.8 Mercury Concentrations Over Water and Land

Mercury measured over land surfaces is generally higher than levels measured over water surfaces. The cycle of mercury release by evaporation or microbial action and deposition by precipitation, impaction or adsorption between the soil and air results in higher mercury levels near land surfaces (2,28). Various terrestrial sinks such as peat moss (65, 90), humic soils (2), and certain clays (91) would no doubt preconcentrate all forms of mercury. Measurements above high mercury containing humus soils range from 20 - 200  $\text{ng.m}^{-3}$  compared with background levels of 5  $\text{ng.m}^{-3}$  (4). Mercury concentrations measured over non-mineralized land (2-9  $\text{ng.m}^{-3}$ ) (8) are insignificant compared with the relatively large concentration near mineralized and mercury mining areas [up to 20,000  $\text{ng.m}^{-3}$  (28)]. Direct comparisons of mercury

concentrations have been attained between air over land and air over oceans. Some measurements from ships and in coastal areas have shown increased mercury levels when the wind blows from the land. For example, the average concentration of mercury measured in the southwest Atlantic increased from 15 to 80  $\text{ng.m}^{-3}$  when the wind blew from the land (12). Similarly, measurements on the California coastline indicated an increase in mercury levels (2 to 20  $\text{ng.m}^{-3}$ ) due to the change in wind direction from over the ocean to over industrialized land (48).

Deep sea ocean measurements have shown relatively lower mercury levels than obtained on land or near the coastline. Total mercury concentrations which were observed at mid-day around Cape of Good Hope and at a distance from the African east coast ranged from 1.8 to 3.8  $\text{ng.m}^{-3}$  total mercury and were about a factor of two to five lower than concentrations measured in the English Channel at the start of the voyage (81). No measurements have been found in this review for atmospheric concentrations in very remote polar regions.

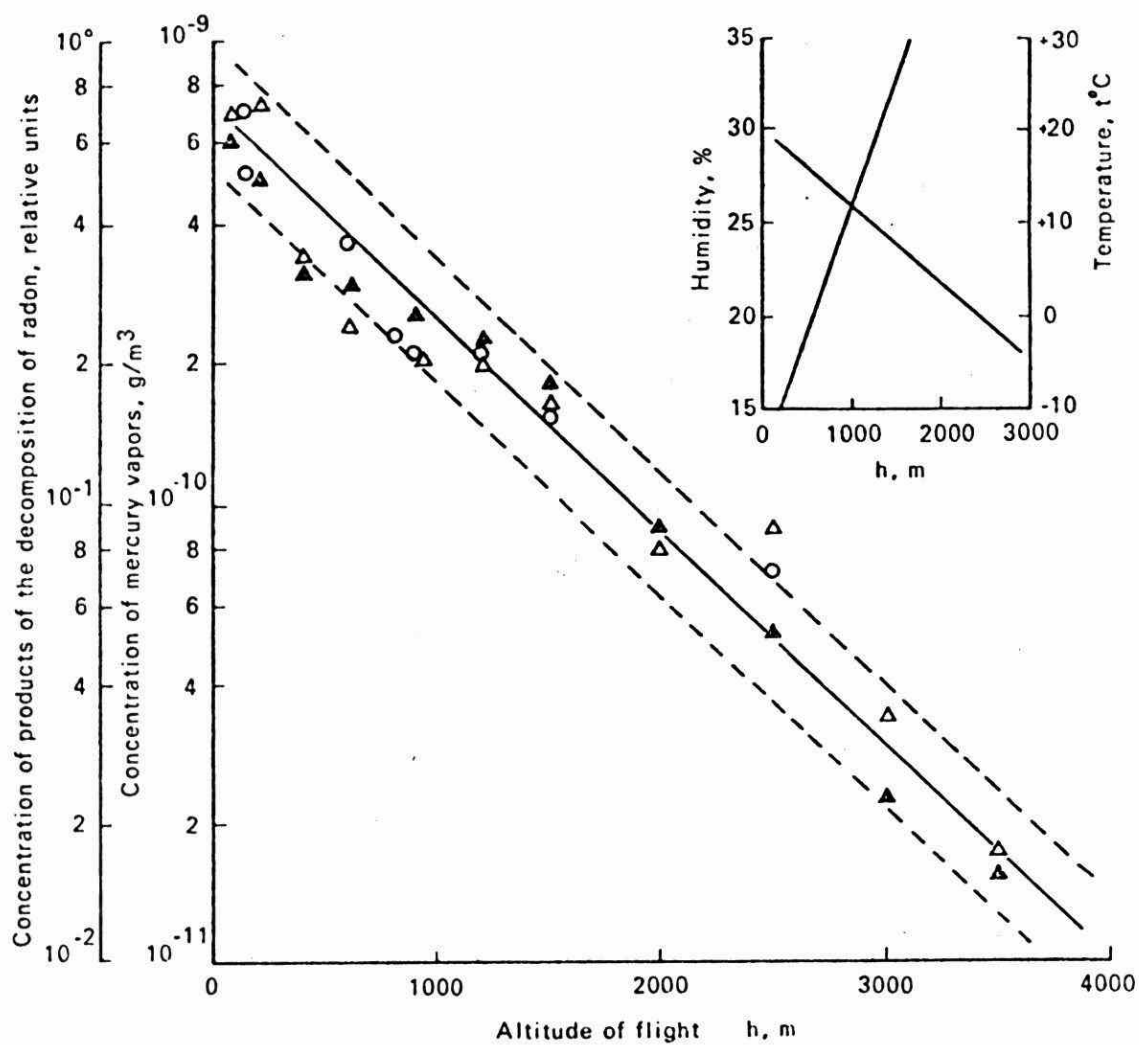
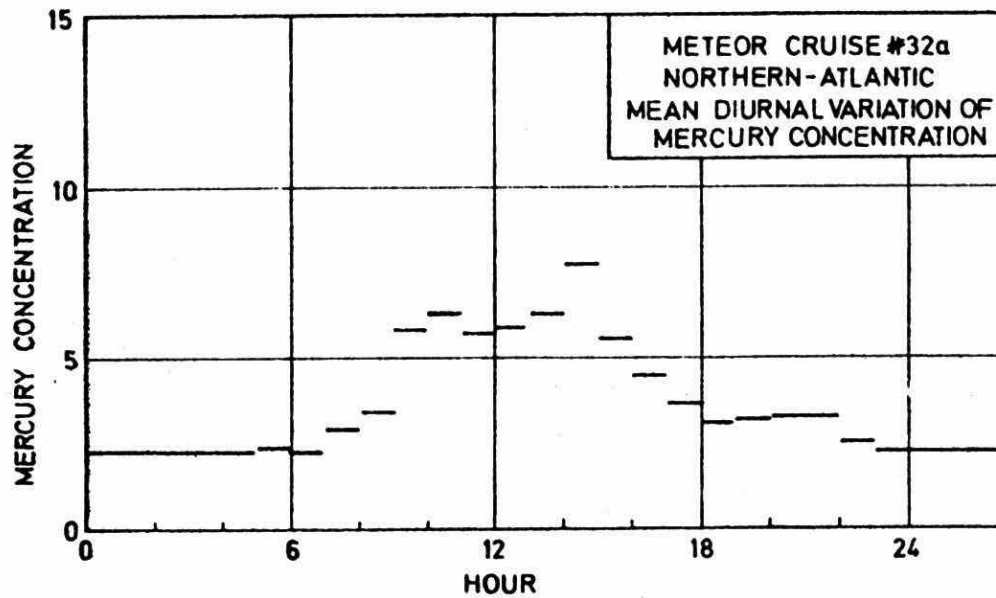


FIGURE 3 - THE ALTITUDE DEPENDENCE OF THE CONCENTRATION  
IN THE ATMOSPHERE OF MERCURY VAPOUR

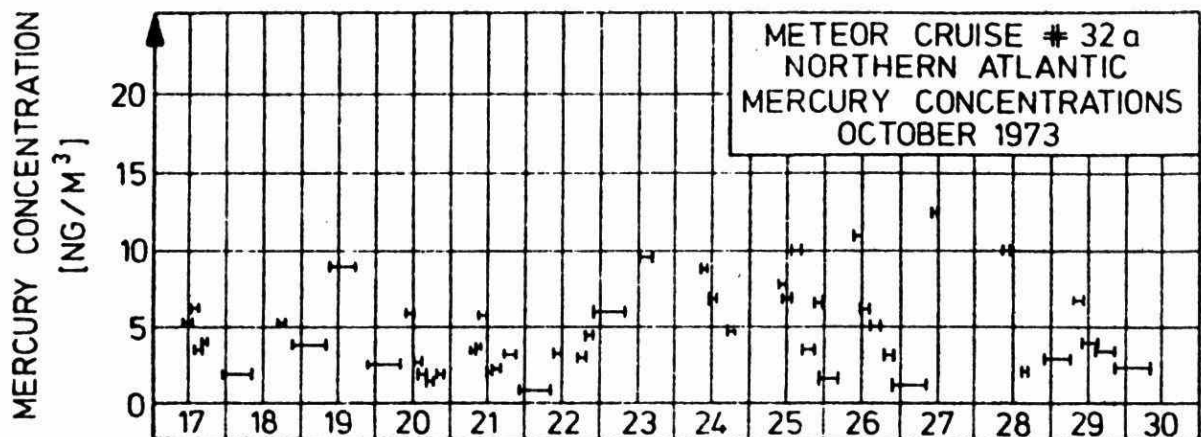
From reference (52)

FIGURE 4a MERCURY CONCENTRATIONS IN AIR MEASURED DURING  
METEOR CRUISE No. 32a OVER THE NORTH ATLANTIC



From reference (53)

FIGURE 4b DIURNAL VARIATION OF THE HOURLY AVERAGE MERCURY  
CONCENTRATION



From reference (53)



**TABLE 5** Summary of Current Data on Atmospheric Mercury Levels for Various Locations

	Range	Mean
	(ng/m <sup>3</sup> )	
<b>A. Remote and Rural Areas</b>		
Oceanic		
Particulate	< 0.005-0.06	<0.15
Vapor	0.6-0.7	0.7
Non-mineralized terrestrial		
Particulate	< 0.005-1.9	0.15
Vapor	1-10	4.0
Volcanic		
Particulate + vapor	20-37,000	—
Mineralized terrestrial		
Particulate + vapor	7-20,000	—
<b>B. Urban Areas</b>		
Particulate	< 0.01-220	2.4
Vapor	0.5-50	7.0
<b>C. Industrial*</b>		
Vapor	7-5,000,000	—

\*These measurements include chlor-alkali plants, thermometer factories, smelters, and mercury mines.

From reference (6)

TABLE 6 SUMMARY OF CALIFORNIA ATMOSPHERIC MERCURY MEASUREMENTS

Site	Date <sup>a</sup>	Time	Wind	Mercury Background Level, ng/m <sup>3</sup>	Mercury Peak Value, ng/m <sup>3</sup>	Comments
<u>Natural Sources</u>						
Abbott Mine	Feb. 12	P.M.	E	0	470	Low population density
Clear Lake	Feb. 12	P.M.	E	0	150	Resort area, low population density
	April 2	P.M.	W	0	200	
The Geysers	Feb. 15	P.M.	W	200-800	28,100	Rural resort area
New Almaden	Jan. 4	P.M.		0	1,500	Rural
	March 24	P.M.		5-15	449	
<u>Cultural Sources</u>						
Berkeley	March 22	A.M.	W	10	800	Light industrial-residential
	March 24	A.M.	W		449	
	March 26	P.M.	W	10	154	
	March 30	P.M.	W	0	1,050	Downwind of landfill
Oakland-	March 30	P.M.	NW	0	196	Light industrial
Emeryville	April 5	P.M.	W	0	668	Industrial complex
	April 6	P.M.	W	0	110	Downwind of STP flare
					700	Industrial area
Pittsburgh	Feb. 11	P.M.	E	50	1,000	Industrial area
	Feb. 12	A.M.	NW	0	0	On boat
	Feb. 25	A.M.	N	0	10	Residential
	March 22	P.M.	WNW	5	4,141	Industrial-residential
	April 1	A.M.-P.M.	N	0		
San Francisco	March 18	P.M.		0	278	Commercial area, quicksilver products
	March 19	A.M.		0	152	
	Jan. 19-26	A.M.-P.M.		0	100	Ambient measurements,
	April 7,8	A.M.-P.M.		0	35	financial district
Richmond	March 29	A.M.	NW	5	1,400	Residential, near primary school
		P.M.	W	5	2,000	

Source: Jepsen, 1973. (55)

<sup>a</sup>Date not given, probably 1971. From reference (6)

TABLE 7 - REGIONAL VARIATIONS IN SPECIATION OF  
ATMOSPHERIC MERCURY IN TAMPA, FLORIDA

Station	Date	Time	ng/m <sup>3</sup> of						Remarks
			Hg <sub>a</sub> <sup>a</sup>	Hg(II) <sup>a</sup>	MMC <sup>a</sup>	Hg <sup>a</sup>	DMM <sup>a</sup>	Σ	
1	3 Aug. 73	07h45-08h15	2	24	15	4	0	45	Wind, calm; 25°C
	3 Nov. 73	07h05-09h13	0	0.8	1.0	0	0	1.8	Wind, calm; 19.5°C
2	3 Aug. 73	08h14-08h44	1	7	19	3	0	30	29°C
	3 Nov. 73	11h25-13h31	0	1	0.2	2.7	0	3.9	25.5°C
3	3 Aug. 73	12h21-12h51	2	0	0	7	0	9	Wind, SE 5 Kt; 31°C; >5000 vehicles/hr on I-75
	3 Nov. 73	13h12-15h12	0	Trace	Trace	2	0	2	Wind, NE 2-8 Kt; 23.5°C
4	3 Aug. 73	11h20-11h50	7	0	8	3	0	18	33°C
	3 Nov. 73	07h27-09h35	0	5.8	0.5	3.7	0	10.0	Wind, E 1-2 Kt; 20.5°C
5	3 Aug. 73	13h15-13h45	4	19	0.5	2	0	25.5	34°C
	3 Nov. 73	10h35-12h41	0.2	7	0.4	4.4	0	12	Wind, NE 2-5 Kt; 25°C
6	3 Aug. 73	12h08-12h38	13	0	3	4	1	21	Wind, SE 5-10 Kt; 34°C
	3 Nov. 73	10h12-12h20	0	Trace	0	2.4	0	2.4	Wind, NE 5-7 Kt; 24°C
7	3 Aug. 73	08h50-09h05	3	11	59	7	3	83	Wind, S 10 Kt; 28°C
	3 Nov. 73	07h42-09h32	0	0.4	0	4	0.3	4.7	Wind, E 1-10 Kt; 22°C
8	3 Aug. 73	09h34-10h09	7	220	22	49	0	298	Wind, SE 5 Kt; 29°C
	3 Nov. 73	07h25-09h47	0.5	0.8	Trace	14	0	15.3	Wind, E 4-10 Kt; 21°C
9	3 Aug. 73	10h27-10h57	1	16	11	5	0	33	Wind, SE 10 Kt; 30°C
	3 Nov. 73	10h16-12h23	0.5	1.5	0.3	5.6	0	7.9	Wind, E 4-8 Kt; 24°C
10	3 Aug. 73	07h53-08h23	7.5	0	119	0	1	127.5	Wind, SSE 5-10 Kt; 26°C
	3 Nov. 73	07h50-09h54	0	0	2.8	5	0.2	8	Wind, ENE 1-3 Kt; 20.5°C
11	3 Aug. 73	11h12-11h42	0	13	22	5	0	40	Wind, SW 5 Kt; 30°C
	3 Nov. 73	10h32-12h22	0.1	0.3	0	3.3	0	3.7	Wind, NNE 5-10 Kt; 25°C

<sup>a</sup> Precision of data is ±6% (1 σ). <sup>b</sup> 3 August—1-hr pumpings; 3 November—2-hr pumpings. For precision, see text.

From reference (73)

TABLE 8 - ELEMENTAL AND TOTAL ATMOSPHERIC MERCURY  
CONCENTRATIONS IN THREE NORTH CAROLINA CITIES

Date 1972	Location	Concentration, ng/m <sup>3</sup>		
		Total	Elemental	Total Minus Elemental
October 3 4 5 6-8	Cary NC	6.0	6.0	0.0
		6.9	6.8	0.1
		8.1	6.1	2.0
		7.7	5.7	2.0
October 3 4 5 6-7	Durham NC	3.8	4.7	-0.9
		4.3	4.4	-0.1
		6.9	4.8	2.1
		5.3	3.5	1.8
October 3 4 5 6-9	Raleigh NC	5.7	6.0	-0.3
		6.4	6.8	-0.4
		5.9	5.8	0.1
		4.2	4.1	0.1

From reference (5)

## 5. THE SAMPLING AND ANALYSIS OF ATMOSPHERIC MERCURY

Analytical techniques for the measurement of trace concentrations of mercury in environmental and biological samples have been the subject of both specialized articles (92) and chapters within more extensive reviews of mercury as an environmental contaminant (2,3,12,93,94,95). Atomic absorption spectrophotometry (AAS), which is the most commonly used analytical technique, has been reviewed separately (96,97,98). Since it will be the principal analytical technique in the current programme, this section of the review will concentrate on the application of AAS procedures to the measurement of atmospheric mercury and exclude other techniques such as neutron activation analysis or X-ray fluorescence spectroscopy.

Three categories of sample are generally collected in an air monitoring programme:

- (a) Solid samples (particulates, aerosols and dustfall)
- (b) Liquid samples (precipitation, including snow)
- (c) Vapour phase samples

Important factors in a trace analytical study are both the sampling efficiency and the accuracy of the measurement process for each type of sample and these are considered in the following sections.

### 5.1 Solid Samples

This category includes both particulate mercury compounds and particulate bound mercury. Aerosol or particulate samples generally have been collected and analyzed for mercury content as part of multi-element studies using high volume sampling procedures (cellulose or glass fibre filters) and simultaneous multi-element analytical techniques such as neutron activation analysis (56,67,99,100,101). More specific studies on the measurement of mercury have also used glass fibre high volume filters (69,102) although other investigators have included membrane filters (55, 74,103) or glass fibre filters (46) as part of multistage sampling trains for speciation studies. These latter applications have involved lower sampling rates. It is suspected that erroneously low levels of mercury on

aerosols may be obtained under high volume sampling conditions due to losses from the high ventilation rates (5,99).

Acid digestion/oxidation of the particulate samples collected on filters has been undertaken using modified procedures for the digestion of sediment samples for mercury analysis (104-106). Routine cold vapour AAS using reduction/aeration (107) was used for subsequent quantitation of the mercury (69), although an intermediate entrapment of the mercury vapour on silver wool was also preferred (102). Anderson and Smith (69) found that their acid digestion procedure (106) was not satisfactory for the analysis of slags and flyash and hence they used thermal volatilization/silver wool amalgamation for these samples. Since the composition of air particulate samples may vary widely, analytical procedures based on the release of mercury from the solid matrix by heating, and intermediate entrapment by amalgamation prior to AAS analysis, may be more accurate than acid digestion procedures. The former technique eliminates problems resulting from reagent blank levels, and by selecting a compatible filter material, the preheating of the filters can result in low background concentrations in thermal methods (46). Another benefit from the use of the thermal technique is improved detection limits due to the amalgamation stage acting as a preconcentration step prior to analysis.

## 5.2 Liquid Samples

The sampling of precipitation (rain and snow) as part of a mercury monitoring programme introduces new problems which have been considered by Matheson (12) but for which solutions have yet to be found. In addition to the basic concern regarding the stabilization of the mercury species in aqueous solution, some of the unknown factors which will be encountered in a monitoring programme will relate to,

- (a) the selection of container materials and preservation reagents most compatible with the mercury,
- (b) the method of addition of the preservative into a container as required,
- (c) the stability and tendency of the preservative to be lost by volatilization under typical ambient temperatures and wind conditions,

- (d) event sampling vs interval sampling,
- (e) the contamination problems at sampling sites (windborne dust, insects, etc.)

Although mercury levels have been reported for rainfall (see Section 4.7) there is little information given as to the method of collection or the preservation procedures, if any. The sampling of precipitation is the subject of a current study (108) which is examining the influence of container material and preservation reagent on the collection efficiency and stabilization of selected mercury species (inorganic and organic) for subsequent analysis of the samples in a laboratory distant from the sampling site. The stabilization of natural water samples for mercury analysis has been the subject of several recent articles (109 - 113), which lead to improvements in stabilization procedures. The emphasis in these studies was, however, on the preservation of inorganic mercury in natural water samples for their collection and transfer in sealed bottles to a laboratory for subsequent analysis. Atmospheric precipitation sampling introduces several additional problems. For example, larger sampling containers used to prevent splashing losses during collection result in the ratio of sample volume to headspace volume in the covered containers being much greater than in samples collected in bottles. Similarly, the ratio of surface area to sample volume is much greater which may lead to more efficient adsorption of mercury on to container surfaces. One study in the above group of stability tests (109) included methylmercury chloride and obtained satisfactory results. However, in another study (114) using sea water as a matrix, it was found that in solutions acidified to pH 2.5, nitric acid was much less effective a preservation reagent than hydrochloric acid for the stabilization of methylmercury chloride. It would appear that stabilization of precipitation samples still warrants considerable attention.

The analysis of mercury in precipitation samples can be undertaken by existing methods for the analysis of mercury in water samples (115). Typical detection limits are 0.02 - 0.03 ng Hg/ml (ppb) based on a sample volume of 50 - 100 ml. Blank reagent levels influence the detection limit but can be controlled by efficient quality control.

### 5.3 Vapour Phase Mercury

A large proportion of airborne mercury is considered to be present as volatile mercury species such as elemental mercury, vapour phase mercuric chloride, methylmercury compounds, ethylmercury compounds, phenylmercury compounds and dimethylmercury compounds. It is essential for any monitoring programme that a method be employed which can efficiently measure the total vapour phase mercury concentration in the atmosphere and at the same time it is desired to achieve limited speciation of the mercury. In reviewing the literature these goals have been borne in mind.

Since background levels of mercury vapour ( $< 10 \text{ ng.m}^{-3}$ ) are usually at or below the detection limits of most analytical instruments based on atomic absorption, a preconcentration step is required. This step can also serve as a purification procedure to separate the mercury species from other atmospheric contaminants which might interfere in the measurement process. The sampling technique should also be capable of collecting all volatile forms of mercury whether organic or inorganic. The two general types of collection systems are based on either liquid or solid collection media.

#### 5.3.1 Liquid Impingement

The most popular absorbing solutions are acid permanganate (116, 117) and iodine monochloride (118). Acid permanganate has been used for the measurement of ambient mercury in addition to mercury in stack emissions (119, 120). It is a very efficient absorbing medium for inorganic and elemental mercury. Whilst acid permanganate shows good entrapment of methyl and ethylmercury chlorides (54, 121), it is not considered satisfactory for the quantitation of these compounds due to their sensitivity to oxidation by the permanganate. Dimethylmercury vapour was not retained by acid permanganate in the work done by Henriques and Isberg (54).

Iodine monochloride is a highly efficient collector of inorganic mercury along with methyl and ethylmercury species (118). It has been tested for ambient air measurement (122) with satisfactory results at loadings of 0.9 g Hg/15ml iodine monochloride solution (0.1N). However, iodine monochloride was found to suffer from high and irreproducible blanks (123). Both of these liquid absorbents have higher capacities than amalgamation



techniques (122) but this is not a major criterion in selecting a procedure for ambient air monitoring.

Other liquid absorbents which have been tested include carbonate/phosphate solution for ethyl and methylmercury entrapment (121). These authors used a sequential combination of this solution and acid permanganate solutions to separate organomercury compounds from elemental mercury in air samples.

#### 5.3.2 Solid Adsorbents

The use of liquid reagents in a procedure results in considerable emphasis on the reagent blank levels and rigorous quality control is required for consistently good detection limits. For this reason, collection procedures based on solid adsorbents have received considerable attention. They have included activated carbon (124,125) hopcalite, (126) cadmium sulphide impregnated pads (116,127,128,129), manganese dioxide (130), copper (131) and noble metals. With the exception of hopcalite and manganese dioxide, all of these procedures are based on the subsequent heating of the collector to release the mercury for its measurement by AAS. Analytical techniques for hopcalite and manganese dioxide collection use acid dissolution of the collecting material and normal reduction/aeration (107) for AAS quantitation. Hopcalite was recommended for collecting mercury vapour in the workplace where higher concentrations are encountered (132,122).

Activated carbon is reported to give poor mercury recoveries (122, 123). However, preheated activated carbon was found to give quantitative collection of mercury, methylmercury and dimethylmercury (133). Field testing (134) of a preheated activated carbon collection system (135) yielded less conclusive results. The ability of activated carbon to adsorb organic compounds which might subsequently interfere in the measurement of the mercury upon thermal volatilization, does not recommend its use for ambient mercury measurement.

Noble metals are the most prevalent type of solid collection systems and are based on the amalgamation of the mercury with a metal and its subsequent release by heating for AAS measurement. Gold and silver are the most popular collectors. Platinum efficiently retains mercury and has been used (136), but requires much higher temperatures in order to effect the



release of the mercury compared to gold (137). Considerable variation exists in the physical form of the adsorbing element as used by different investigators. Gold has been used as wire and foil (137,138,139,140), particles or chips of gold (141) or as thin layers of gold deposited on either glass beads (46,142), quartz (143) or on sieved ceramic powder. Similarly, silver has been used as wire, gauze or wool (46,48,102,145,149,150), or as silver deposited as fine layers on Chromosorb P (151).

Both silver and gold are highly efficient collectors of elemental mercury. Organic forms of mercury are less well retained by silver (46) and it was observed that dimethylmercury was not adsorbed by silver. Although methylmercury was retained, it was slowly released when air was passed over the adsorbent at 20-30°C for more than 5 - 10 minutes. Conversely, Eberling (53) noted that silver wool retained dimethylmercury with an efficiency of 76% (when present in samples at concentrations of 1-2 mg.m<sup>-3</sup>). Gold has the capacity to retain both inorganic and organic forms of mercury (46,54).

Factors which are important in the selection of a metal adsorbent for ambient air monitoring relate to the available surface area of the collector and the effect of atmospheric constituents on the quality of the surface. Both factors influence the adsorption efficiency of a particular collector and may be particularly important in the case of the organomercury species which are less strongly retained by these collectors. Copper is very sensitive to atmospheric oxidation and is not therefore of significant value. Gold is less sensitive than silver to atmospheric oxidation or reaction with other impurities such as sulphur dioxide and hydrogen sulphide (152). Hartley and Devine (142) found that neither SO<sub>2</sub>, H<sub>2</sub>S, nor NO<sub>2</sub> at concentrations of 10 ppm interfered with the adsorption efficiency and retention of mercury by a gold collector. These authors were, however, using pyrolysis of the air sample prior to its coming in contact with the collector. Using this system they also detected no interference from acetone, benzene or ethanol at concentrations > 60 ppm. H<sub>2</sub>S at high concentrations (200 ppm) did foul the absorbing surface but the interference was reversible.

Improvement in the available surface area of a collector has been achieved by depositing gold or silver as thin layers or more evenly sized spheres (glass or ceramic). The chemical procedures used to form the coated beads are based on the reduction of brown gold chlorides (153) or the silver mirror reaction. It was noted (142,144) that the deposition of gold on glass beads resulted in very uneven distribution of the gold on the surfaces. Scullman and Widmark (144) felt that they achieved significant improvement by reducing the amount of gold deposited and by using sieved ceramic material ground to 60-72 mesh. Hartley and Devine (142) used an organometallic coating material (Bright Gold Q-Engelhard) to achieve more uniform coatings on glass beads (60-80 mesh). The use of spherical particles allows more even packing and optimization of available surface. Scullman and Widmark (144) encountered memory effects in the use of gold chips or foil and showed that as the amount of gold deposited onto particles was increased there was significant difference in the release of mercury from the amalgam upon heating.

Based on the differing adsorption capacities of collectors such as gold or silver, attempts have been made (46,54) to develop sampling trains which will allow the speciation of mercury in air samples. To obtain the separation of different mercury species, additional adsorbents were introduced and these included Chromosorb W.-30% SE for the retention of  $\text{HgCl}_2$  and Chromosorb W treated with 0.05M NaOH for the selective retention of methylmercury (46). Henriques and Isberg (54) found that coating gold with a thin layer of gold silicon alloy rendered it inactive towards organomercury compounds but still highly effective for elemental mercury.

Amalgamation techniques have also been used in procedures developed for the measurement of total mercury in air which are based on the use of pyrolytic techniques to convert all organomercury compounds to elemental mercury for subsequent entrapment in gold collectors (142). Comparison of the mercury content pyrolyzed and unpyrolyzed samples may suffice to measure the organic mercury content of the air. These authors reported recoveries of greater than 95% for the analyses of organomercury species by this procedure. Pyrolysis generally involves the heating of the air sample to temperatures of 650 - 700°C with or without the presence of a

catalyst such as platinum (54) or gold (138) which assists in the oxidation of organomercury compounds. It is important that the pyrolysis temperature be high enough ( $> 500^{\circ}\text{C}$ ) to dissociate any  $\text{HgO}$  which forms when mercury is heated in air (at temperatures greater than  $300^{\circ}\text{C}$ ) and the cooling of the mercury bearing air should be done rapidly (54).

An important aspect of the use of an amalgamation technique is the subsequent release of the mercury and measurement of the concentration. In general, AAS is used, although one group has used a D.C. arc emission (46). Factors such as heating rates, purge gas flow rates, weight and type of adsorbent present, will influence the instrument response. The calibration of amalgamation systems is usually achieved by injecting known volumes of mercury saturated air into the system. Corte and Dubois (148) observed that if the mercury was generated into a silver amalgam system by reduction/aeration of a mercuric salt, the calibration curve when compared with the curve for the same amounts of mercury injected as mercury vapour showed a linear response in both instances but with significantly different slopes. It appeared that some of the mercury in the mercury vapour generated by reduction was not available for amalgamation.

Techniques based on amalgamation show good reproducibility and samples once amalgamated show good stability. As with all mercury analytical procedures, care is required to ensure low blanks, activation of collector surfaces and sealing of sample tubes to prevent contamination during transit.

In most instances the technique is based on a single amalgamation step prior to AAS measurement. The introduction of a double amalgamation approach (140) was used to assist in freeing samples of interfering compounds. In the case of atmospheric monitoring, it may be beneficial to use the double amalgam approach where one collector is a constituent of the AAS system. The field adsorbers may be returned to the laboratory and the mercury transferred to the system collector for subsequent analysis. It is envisaged that this will serve as both a purification procedure and allow more consistent sample introduction into the AAS. Measurement of analytical responses is based on either peak height or peak area although the latter approach is recommended (147).

#### 5.4 Instrumental Methods

Background mercury concentrations can be less than  $1 \text{ ng.m}^{-3}$  in the atmosphere. Only in very exceptional circumstances, such as being downwind of a mercury emitting source will levels higher than  $10 \text{ ng.m}^{-3}$  be recorded. Instruments that are sufficiently sensitive to make meaningful measurements at these concentrations fall into two groups:

1. Instruments that pass atmospheric gases over an adsorber of mercury, such as gold or silver, for a certain period of time. The flow of gas is then stopped and a slower flow of inert carrier gas is passed over the collector into a suitable UV spectrophotometer. The collector is heated to several hundred  $^{\circ}\text{C}$  either by passage of current through the collector or by placing the collector within a powerful RF field. The adsorbed mercury is flushed into the spectrometer and its absorption and hence concentration determined quantitatively. A number of currently available instruments (Geomet Monitor, APTC Mercollector) are based upon this approach.

The main problem with this type of instrument is that the typical time for flow of atmospheric gases to deposit sufficient mercury for an adequate measurement is long and of the order of several minutes to several hours, depending on the concentration of mercury in the atmosphere sampled. These systems are relatively difficult to calibrate since the calibration gas must be supplied for periods at least as long as the sampling period to enable both collection and evolution efficiencies to be evaluated. Contamination of collectors has to be very carefully controlled.

Compromises have to be made in the collector design. The larger the area of collection and the more close-packed is the adsorbing material, the better the collection efficiency. Unfortunately the electrical power required to heat the collector sufficiently will increase and a larger pressure drop across the collector will exist.

The advantages of this type of system are:

- it can be built relatively inexpensively
- it can be very specific for mercury without complex instrumentation
- by extending the sampling interval to long period, very low levels of mercury can be detected.

A typical application of this type of measurement is that of Azzaria (155) in which measurement of mercury in soil and air were used to explore for ore deposits in four areas of Quebec.

Other instruments which accumulate mercury for later determination include the quartz crystal microbalance (156) in which mercury vapour is adsorbed on a gold film supported on a quartz crystal. The weight of mercury adsorbed is determined from the change in resonant frequency of the crystal. A somewhat similar technique in which the change in resistance of a thin gold film due to adsorption of mercury is measured has also been described (157). This is now a commercially available instrument (Jerome Instruments). If this type of instrument is to be used for ambient atmospheric mercury levels it seems likely that extremely long sampling periods would be required to deposit a sufficient weight of mercury to achieve adequate sensitivity.

2. Instruments that detect mercury in "real time". These instruments determine mercury by the absorption of ultraviolet radiation from a mercury discharge lamp. Where the various instruments differ is in the method used to resolve mercury from the many other gaseous and particulate species that absorb or scatter ultraviolet light. The evolution of these instruments was reviewed by Robbins (158) in 1972. The main problem has been the development of an adequate electro-optical system for the measurement of concentration changes equivalent to a five to ten absorbance units in instrument packages rigid and sturdy enough for installation in vehicles or aircraft.

The main impetus for the design of these more complex instruments has been the need for fast response in order to detect emission

sources (ore deposits, for example) in mobile surveys. Typical response times are of the order of a few seconds. For stationary measurements lasting several hours or days, problems arise with instrumental zero-drift which is mostly temperature induced. Where such longer measurement intervals permit their use, specific mercury filters (r.g. porous filter material coated with palladium chloride) are used to establish a baseline in the spectrometer system.

## 6. ATMOSPHERIC TRANSFORMATION AND TRANSPORT

The various sources of mercury, both natural and anthropogenic, and the resulting atmospheric concentrations have been discussed in Sections 3 and 4. The transport and transformation of mercury in the environment depends on many physical and chemical factors and the availability of other chemical species with which it can react (159). Thus, the behaviour of mercury in the environment is an extremely complex phenomena and some of the more important features are (5):

- all compartments of the environment contain traces of mercury
- a variety of forms and compounds of mercury can exist in nature and as a result of mans activities
- complex transformation processes can occur in all compartments of the environment
- the impact of anthropogenic activities must be considered relative to the natural geochemical cycle
- the transport of mercury in the food chain occurs via a complex set of chemical transformations.

This discussion is limited to a consideration of the general features of atmospheric transformation and transport and the important role which these processes play in the overall environmental cycle of mercury.

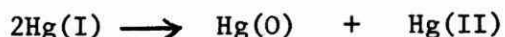
### 6.1 Atmospheric Transformations

Several reviews (2,4,5,6,12,17,25,28) have discussed the chemical and physical transformations of mercury which can take place in the environment. In an earlier review, Kothny (25) has evaluated mercury levels in terms of an equilibrium between the mercury contents in the atmosphere, particulate matter and rocks. The assumption in this work that most mercury is adsorbed onto particulate matter has been discounted by more recent studies (Section 4). A paper by Therkelsen (160) describes the aquatic chemistry of mercury and the mercury cycle in the aquatic environment, and this subject also has been discussed in considerable detail in other recent reviews (2,5,161). Peakall and Lovett (17) focused their attention on mercury contamination of the food chain and concluded (in 1972) that direct human health hazard of environmental



mercury appeared to be limited to those persons for whom fish is a dominant part of their diet. They also concluded that it should be possible to reduce greatly the amount of mercury being emitted from anthropogenic sources directly to the fresh water and land environment, and it is reasonable to say that this has been achieved in the intervening period. They expressed a justifiable concern over the probable difficulty of reducing the contribution arising from fossil fuel combustion.

Information on the forms in which mercury exists in the atmosphere (Section 4.1) is important in order to understand its distribution, transport, deposition and ultimate contamination of the food chain. Mercury is found in three valence states [Hg(0), Hg(I) and Hg(II)] and forms hundreds of compounds, both inorganic and organic. Elemental mercury, Hg(0), reacts with a wide variety of oxidizing agents to form Hg(I) and Hg(II) compounds and in the environment conversion from one form to another takes place (5) according to the disproportionation reactions,



The form which predominates depends upon the prevailing conditions and important factors are redox potential, the electrical potential-pH relationship, temperature and the concentration of major ions in the solution (6). Four basic reactions are involved in the overall mercury conversion cycle:

- (1) conversion of Hg(0) to Hg(II)
- (2) conversion of inorganic Hg(II) to methyl mercury
- (3) conversion of phenyl mercury to methylmercury
- (4) conversion of alkoxyakyl to Hg(II) or Hg(0)

The role of each of these reactions in the cycle of mercury interconversions in nature is summarized in Figure 5 and is discussed in further detail in the recent National Academy of Sciences (NAS) review (6) and elsewhere (e.g. 17, 25). Before considering the transformation processes occurring in the atmosphere, the biological conversion of inorganic mercury to organic mercury



in various segments of the biosphere should be noted as the key element in the distribution, transport and bioaccumulation of mercury in the environment.

Mercury is emitted to the atmosphere in several forms but it is now reasonably well documented (Sections 3 and 4) that elemental vapour is the predominate form which is emitted to, and exists in, the atmosphere. This elemental mercury arises from a number of sources (12):

- natural mantle degassing
- volcanic emissions
- mining and smelting operations
- fossil fuel combustion
- municipal and industrial incineration
- losses from many industrial processes, including chlor-alkali plants

Organomercury compounds are the other important form of atmospheric mercury and arises primarily from biological processes.

Important examples include:

- emissions from soils, marshland and water bodies
- plant life
- sewage treatment plants

These volatile organomercury compounds which are produced by biological processes in water and sediments are believed to evaporate rapidly (11) and have been measured near polluted bays (73) and near waste water treatment plants (71) in substantial amounts.

Since elemental vapour is found to be the major atmospheric form in most studies (Section 4) it appears that the decomposition of these organomercury compounds to elemental mercury in the atmosphere could be an important part of the mercury cycle. However, the available information does not appear to establish clearly the overall relative importance of elemental and organomercury emissions to the atmosphere as a result of soil

degassing and this ratio will, of course, determine the importance of organomercury decomposition processes in the atmosphere. Mercury (II) inorganic compounds were measured in the vapour phase by Johnson and Braman (71,73). Possible sources of these inorganic compounds could include direct volatilization from soils and water, direct industrial emissions, and reactions in plumes from fossil fuel combustion, but no other references on the measurement of these species have been found in this review. The conditions in most plumes will be amenable to chemical interaction to form salts or oxides since  $\text{SO}_2$ , and subsequently sulphate salts and  $\text{H}_2\text{SO}_4$ , will almost always be present. Other anions and metallic oxides with some catalytic activity will be present and thus the possibility of the relatively fast conversion of elemental mercury to inorganic salts or oxides exists.

The ability of mercury to act as an energy transfer agent for photochemical reactions has long been recognized (162). Williston (48) monitored mercury levels in the San Francisco Bay area continuously for 2 years and noted that high mercury levels always coincided with high smog levels. No doubt mercury could act as a catalyst to promote atmospheric photochemical reactions, either as an energy transfer agent, or by direct chemical catalysis. However, it is not yet understood (28) what role the organomercury compounds could play, in photochemical mechanisms, nor is it clear that such phenomena are a significant pathway for the atmospheric transformation of mercury. This aspect of atmospheric chemistry does not appear to have received any attention recently, from either the viewpoint of photochemical activity or the cycling of mercury in the environment. Jonasson (3) reported that both organic and inorganic compounds can break down in the presence of sunlight to yield elemental mercury vapour. In view of the probable importance of organomercury emissions from biological processes, it is very likely that this is indeed an important process in the atmospheric transformation of mercury. The possibility that mercury could react with sulphur compounds such as  $\text{SO}_2$ , sulphides and mercaptans has been recognized but not evaluated in any detail (28).

In conclusion, it appears that the decomposition of organomercury

compounds into elemental mercury is an important atmospheric reaction of mercury. Adsorption on particulates is probably less important than previously believed and no information on the composition or reactions of particulate mercury has been found in this review. It is apparent from the literature that a much higher priority has been given to the elucidation of transformation mechanisms in soil, water and the food chain than in the atmosphere. This priority is appropriate in view of the extreme importance of the biological processes which convert inorganic compounds to the more toxic and volatile organomercury species. Nevertheless, the real lack of any significant data base which can be used to define the reactions and transformations of mercury which are assumed to occur in the atmosphere must be recognized and certainly should be a priority area of study in the near future.

## 6.2 Atmospheric Transport

Mercury differs from many other atmospheric pollutants by virtue of the diversity of sources, forms, compounds and sinks which exist in the environment. While it is reasonable to believe that the general concepts of atmospheric transport and deposition models developed for other gaseous and particulate pollutants (67,163 - 180) can be applied to mercury, these complexities must be taken into account. Unfortunately, the present lack of specific experimental evidence on the forms, concentration and reactions of mercury in the atmosphere require many assumptions to be made in devising transport and deposition models and a major objective of subsequent phases of this study will be to provide experimental data on these aspects of the problem.

Mercury emitted to the atmosphere is dispersed by air mass movements and deposited on land and water by dry deposition, rainfall and snowfall and possibly direct contact by vapour. The earlier studies (McCarthy et al in 1970 (4), for example) indicate that the rate of mercury release into the atmosphere is determined mainly by the rate of decrease of atmospheric pressure as a consequence of the earth's breathing process, and that wind, rainfall and snowfall, seasonal variations in temperature and other natural and meteorological factors are important in determining the distribution and transport. The distribution of mercury

in the atmosphere has been discussed in Section 4 and some of the more important features which are pertinent to transport mechanisms are:

- higher levels are found in summer than in winter and presumably reflect increased degassing rates with increased temperature
- diurnal variations occur and appear to depend primarily upon rate of barometric pressure change and temperature
- higher mercury readings have been observed on cloudy and foggy days than on normal days
- high mercury levels tend to concur with smog formation
- cool wet weather generally results in lower than average mercury readings, whereas the reverse is true for warm dry weather, even though daily maximum mercury readings do not necessarily coincide with daily maximum temperature
- mercury levels appear to decrease quite sharply with altitude confirming the probable importance of soil degassing as an important source.

Matheson (12) has recently completed an extensive review of subject areas relating to the atmospheric transport of mercury and concludes that:

- (i) elemental mercury exists primarily as a vapour in air
- (ii) mercury is released from all land and water surfaces and thus natural sources predominate
- (iii) strong local anthropogenic sources have little effect on local deposition rates and are broadly dispersed into the atmospheric reservoir
- (iv) precipitation washout of mercury may not be as effective a deposition mechanism as previously assumed.

The relative importance of natural and anthropogenic sources has been discussed in earlier sections in terms of both emission inventories and global cycle estimates, but perhaps warrants some further

elaboration here. In a number of review papers (7,24,28) the opinion is expressed that soil degassing figures are much too high because of a neglect to take into account the possible cycling of mercury between the soil and the air. Several studies are cited (6,86) which indicate that rainfall washout mechanisms may serve to bring the mercury back to the ground only to be released again to the atmosphere due to the turbulence of impaction. However, contradictions seem to exist as to washout efficiencies and in view of this conflicting evidence, it is possible that mercury may have a significant dry removal component (vapour impact) as well (6). This recycling mechanism, if it exists, means that mercury may be deposited several times before it leaves a continental land mass and thus its effective residence time in the atmosphere may be much longer than has been estimated. On this basis, it may be necessary to revise upwards the relative importance of man's contribution to global mercury cycling from the currently estimated 5 to 30 percent.

For these same reasons there is some doubt concerning the validity of using snow cores to deduce the content of snow at the time it was deposited (181,182). Greenland snow deposits show a much less marked increase in mercury than in lead, for example, and it is possible that the measured mercury concentrations in snow may simply reflect variable proportions of dry plus wet input (6). Matheson (12) attributes the relatively small increase in Hg content of polar ice in post-industrial times to the fact that the polar atmosphere is only loosely coupled with the circulation in lower latitudes.

The definition of global cycles can often be useful in considering the sources, mechanisms of transformation and transport, and sinks of pollutants in the environment. This is particularly so for complex systems for which many details are lacking, as in the case for mercury. Although such models can be criticized for the many assumptions that must be made and the lack of any ability to define effects on a local, or even regional scale, they do provide an initial assessment of the various components and pathways that might be postulated.

Several global mercury models (25,52,183,184) have been developed in recent years and these have been reviewed and an updated model prepared

by the U.S. National Academy of Science (6), utilizing the detailed mercury balance for the United States prepared by Van Horn (20). Although details of calculations and basic assumptions varied among authors several important conclusions were drawn from these earlier studies:

- The atmosphere plays an important role in the mobilization of mercury. The earth-surface to atmosphere flux is several times larger than that occurring between continents and oceans.
- The earth-surface to atmosphere flux seems to involve mainly elemental mercury vapor, whereas the flux between continents and oceans involves inorganic divalent mercury, much of it associated with dissolved and particulate organic matter. In terms of quantity, alkylated forms of mercury do not contribute appreciably to the global mobilization of the element. A biological cycle that involves the transfer of alkylated forms of mercury does however, exist, as mentioned earlier.
- According to various estimates, the residence time for mercury in the atmosphere varies from 5.5 to 90 days, and the proportion of man-made mercury in the atmosphere ranges from 10 to 80 percent.
- Use of mercury by man and subsequent emissions to land, rivers, and lakes, together with increased erosion rates have elevated the mercury content of lakes and rivers by a factor of 2 to 4. Increases in total oceanic mercury concentrations have been negligible. The mercury content of soil appears to have increased by about 0.02 percent.

In the preparation of an updated model, NAS reviewed a number of the assumptions involved in the earlier work and the major points considered were:

- on the basis of the recent evidence that Greenland resources

reflect polar and oceanic deposition rates not influenced by man (see above), atmospheric flux calculations derived from these data were discounted

- estimates of natural mercury flux from the earth's surface to the atmosphere were revised, with lower degassing rates being assigned to oceans than to continents
- the role of washout by precipitation was re-assessed because of the conflicting evidence about mercury concentrations before and after rain events
- information on decreasing mercury concentrations with increasing altitude suggest that previous estimates of the atmospheric mercury pool may have been excessive.

New information on these points was combined with the previous models to summarize current knowledge of the global cycle of mercury. Mercury fluxes and reservoirs were calculated in terms of both a "present day" and "pre-man" framework and these cycles are summarized in Figure 1 and 6, respectively. In the interest of accuracy and completeness, the most important assumptions used in constructing these models are quoted here without change (6):

The mercury deposition rate over polar regions, derived from Weiss et al ('75) is taken to be  $22 \times 10^{-6} \text{ g/m}^2/\text{yr}$ .

A similar deposition rate is assumed for oceanic areas.

If the average mercury concentration in air for these areas is  $0.7 \times 10^{-9} \text{ g.m}^{-3}$ , the deposition velocity is approximately  $10^{-3} \text{ m/sec}$  (wet + dry) (Chamberlain, 1960).

If the deposition velocity remains constant over oceanic shelf areas and continents, the rate of deposition for these areas is  $(1.5/0.7) \times 22 \times 10^{-6} = 47 \times 10^{-6} \text{ g/m}^2/\text{yr}$  and  $(4.0/0.7) \times 22 \times 10^{-6} = 126 \times 10^{-6} \text{ g/m}^2/\text{yr}$ . The assumption that the deposition velocity for polar, open ocean, and oceanic shelf areas is similar seems quite reasonable, whereas the assumption that the deposition velocity over continents is the same remains to be tested.



Using mercury degassing rates measured by McCarthy et al (4), Van Horn (20) conducted a state-by-state inventory of mineralized and non-mineralized areas. From the results, an average degassing rate of  $130 \times 10^{-6} \text{ g Hg/m}^2/\text{yr}$  was calculated for the United States. This rate was assumed to remain the same for all continents. The degassing rates that support the atmospheric mercury concentrations for oceanic shelf, open ocean, and polar regions were then calculated to be  $(1.5/4) \times 130 \times 10^{-6} = 49 \times 10^{-6} \text{ g/m}^2/\text{yr}$  and  $(0.7/4.0) \times 130 \times 10^{-6} = 23 \times 10^{-6} \text{ g/m}^2/\text{yr}$ , respectively. These calculations balance the input rates quite well.

Since no increase in mercury deposition rates has been observed in polar regions, it was assumed that emissions of mercury to the atmosphere from anthropogenic sources would result in increased deposition rates only over continents and oceanic shelf areas. As additional data becomes available this assumption will undoubtedly have to be revised since atmospheric constituents in the northern hemisphere are transported from east to west over considerable distances. From an environmental protection point of view however, this assumption is conservative because it maximizes mercury deposition rates for continental and oceanic shelf areas.

Since there are no data to indicate that degassing rates in oceanic shelf and open ocean areas have increased over the past century, it was assumed that these two areas realized a net increase of  $22 \times 10^8 \text{ g/yr}$  from the atmosphere.

Flux rates between continental, oceanic shelf, and open air masses and between shelf and open ocean water masses cannot be evaluated with current information. Evidence suggests, however, that much of the river-borne mercury is deposited initially in estuarine and continental shelf areas.



Many conclusions derived from the two models are similar to those discussed earlier, but there are some differences as well. The residence times of mercury for the various reservoirs calculated here are: soils, 1000 years; atmosphere, 11 days; oceans, 3200 years; and sediments,  $2.5 \times 10^8$  years. This shorter residence time calculated for atmospheric mercury is at variance with results from several previous models. This discrepancy can only be resolved with additional measurements both for different altitudes and for remote areas. Additional data on atmospheric mercury levels in remote areas would be especially helpful. The model indicates that from 25 to 30 percent of the atmosphere mercury burden is due to man-made emissions.

This update of the global cycle for mercury is an extremely useful framework within which to plan and consider future studies of limited segments of the environment. While many questions remain, such as the net efficiency of washout as a removal mechanism, the possible role of dry vapour contact on water surfaces, etc. an overview is produced and a reasonably consistent set of parameters defined.

A number of studies have been concerned with mercury transport from anthropogenic sources on a more localized scale. One of the first modeling studies to demonstrate that the major portion of mercury emitted into the atmosphere by power plants and incinerators remains airborne for relatively long distances (tens of kilometers) was carried out by Lockeretz (49) in 1974. Using simple atmospheric dispersion and modeling concepts he was able to show that only a small portion of the mercury was deposited locally. Calculations were done assuming both total and no adsorption on particulates in view of the lack of information on adsorption at that time. The results of this study emphasized the importance of considering mercury pollution phenomena on a large scale, even when dealing with strong point sources. The need to give greater attention to area sources (which could contain numerous industrial point sources within a few kilometers of each other) was also noted.

In a recent Norwegian study (54) of background levels in air of lead, cadmium, mercury and chlorinated hydrocarbons, a remarkably clear correlation between concentrations and the direction of air flow was observed, with industrialized and densely populated areas being identified as sources. In Swedish studies (65,83) of mercury fallout from chlor-alkali plants it was concluded that only a small fraction of the total amount of emitted mercury was deposited locally. The major part seemed to be spread over very large areas and probably contributed to global circulation as well as to regional background deposition. Recent U.S. studies have been concerned with the dynamics of mercury deposition at coal-fired power plants (69, 185) and the atmospheric input and origin of selected elements to a watershed in Tennessee (60).

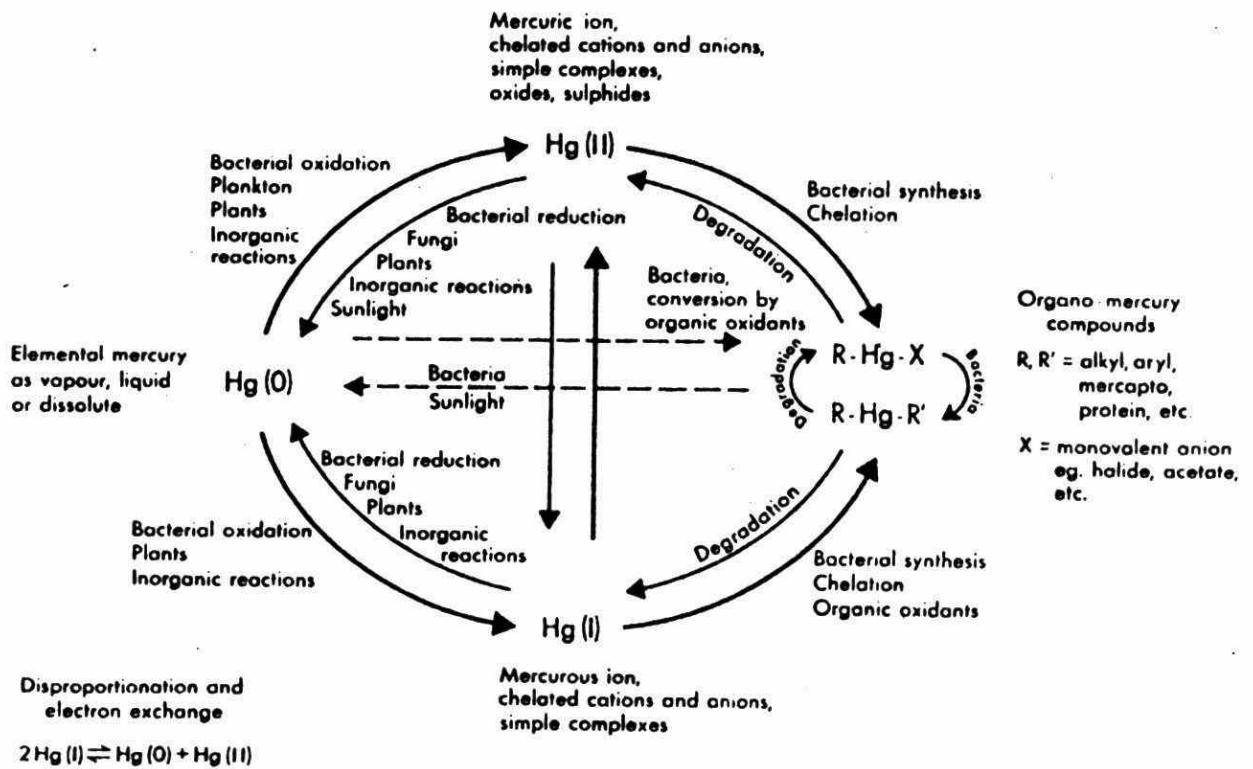
In an unpublished modeling study (24) particular attention has been given to the question of atmospheric recycling of mercury (see above) and it is postulated that the atmosphere could be a major source of mercury to freshwater systems. It is pointed out that if fresh water removes mercury from the atmosphere as efficiently as oceanic water, input from the atmosphere could be substantial while the neighbouring land remains effectively uncontaminated. This possibility of dry mercury vapour impact on water surfaces as an important deposition mechanism has been alluded to by others and it might help to explain the anomalously high mercury concentrations observed in the biota of lakes remote from known sources (81, 11). In recent studies in Northern Quebec, acid precipitation has been proposed as a possible source of mercury in fresh water lakes but no detailed deposition mechanism has been defined. Many questions arise as to the most likely mechanism that might prevail:

- are mercury and acid rain constituents ( $\text{SO}_2$ ,  $\text{SO}_4^{=}$ ,  $\text{H}_2\text{SO}_4$ , etc) merely occurring together in the atmosphere as a result of being emitted from a common source, or sources?
- is the acid rain a more effective washout medium (higher solubility) for the removal of mercury from the atmosphere?
- is dry vapour impact at the lake surface a more efficient deposition mechanism when the pH of the lake is reduced?

- or do other soil/water/biota interactions not within the scope of this study show a pH dependence?

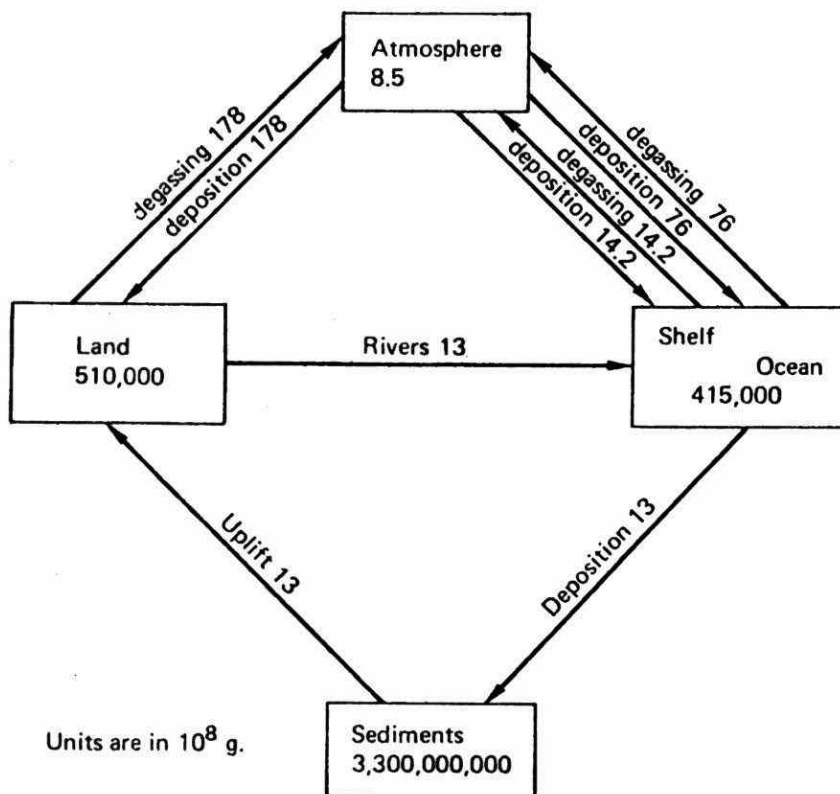
In a recent Swedish study (81) of the possible relationship between high acidity and high mercury content of fish in fresh water lakes there was no evidence to indicate that mercury vapour levels correlated with long distance transported acid constituents. However, a positive correlation was found between mercury content of the air and the surface temperature of coastal sea waters. A hypothetical model for the transport of mercury from this source and subsequent deposition in acid lakes via the atmosphere was proposed and included the theoretical assumption that organomercury compounds could be more effectively dissolved at the air/water interface under acidic conditions.

FIGURE 5 - CYCLE OF MERCURY INTERCONVERSIONS IN NATURE



From Jonasson and Boyle (1971), reference (18)

FIGURE 6 - PRE-MAN GLOBAL CYCLE OF MERCURY



From reference (6)

## 7. CONCLUSIONS

This review of the literature on mercury as an environmental pollutant was undertaken as the first stage of an experimental study to determine the importance of the atmosphere as a medium for the transport of mercury to land and water surfaces in Ontario. It soon became apparent that a much higher priority has been given to the study of mercury in soil, water and biota than in the atmosphere and, consequently, much of what is known of the processes and mechanisms occurring in the atmosphere is based on very limited experimental data. Nevertheless, a fairly consistent, if not detailed, perspective of mercury in the atmosphere has developed and some of the more important features are:

- many sources of mercury exist, and current estimates indicate that man's activities account for 5-30% of total emissions.
- only a small portion of these anthropogenic point source emissions are deposited locally, with the major portion being distributed quite widely and thus becoming part of the continental reservoir. Area source emissions are believed to contribute similarly to background levels.
- a major portion of natural emissions to the atmosphere may occur as volatile and toxic organomercury compounds as a result of mantle degassing and many of the features of the distribution of mercury in the atmosphere confirm the importance of this natural source.
- based on current data, elemental vapour is the major form in which atmospheric mercury exists and thus it is likely that the conversion of organomercury compounds to elemental mercury is an important atmospheric process. Photochemical decomposition could be involved but has not been studied.

- the limited data available indicate that mercury is adsorbed only to a limited extent on atmospheric particulates. The types of atmospheric compounds adsorbed are unknown.
- prevailing atmospheric concentrations of mercury vapour have been reasonably well defined and the lowest concentrations ( $\sim 0.6 \text{ ng.m}^{-3}$ ) occur over the oceans and other remote regions. Continental background levels are in the  $1 \text{ to } 10 \text{ ng.m}^{-3}$  range while typical levels for urban areas are  $2 \text{ to } 60 \text{ ng.m}^{-3}$ . Levels as high as  $600,000 \text{ ng.m}^{-3}$  have been measured downwind of point sources.
- fairly consistent, and quantitative, global mercury cycles have been derived, and the atmosphere is shown to be an important transport medium for the movement of mercury through the environment. According to the most recent estimates, the residence time of mercury in the atmosphere is only 11 days compared with 1000 years for soils, 3200 years for oceans and  $2.5 \times 10^8$  years for sediments.
- the effectiveness of washout by precipitation as a deposition mechanism has been questioned because of conflicting evidence on the extent to which mercury is recycled between the soil and the atmosphere during and after rainstorms. Should this recycling prove to be important, estimates of the relative significance of anthropogenic emissions would have to be revised upwards. The forms of mercury in precipitation are unknown.
- these questions concerning washout also give rise to the possibility that dry vapour deposition on fresh water surfaces could be an important deposition mechanism. Such a mechanism might account for the occurrence of elevated mercury levels in the biota of

freshwater lakes remote from known sources. Some connection between acid precipitation and these elevated mercury levels has been implied but no specific mechanism identified.

The many forms of mercury and numerous reactions which they undergo must be considered in adopting sampling and analytical methods for the trace levels which occur in most environmental samples. Instrumental techniques capable of continuously measuring background levels of mercury now are available. It is concluded that the best available approach to cumulative sampling, capable of differentiating between particulate, elemental and organomercury compounds, would consist of the following:

- particulate collection by low volume filtration
- total mercury vapour collection by pyrolysis in conjunction with noble metal amalgamation
- differentiation between elemental and organic mercury vapour compounds by parallel sampling of elemental vapour only on noble metals (without pyrolysis)
- analysis by atomic absorption spectrophotometry after the release of amalgamated elemental mercury vapour by heat.

While adequate analytical sensitivity is available, many potential problems appear to remain regarding the prevention of contamination and deterioration of precipitation samples. Contamination from extraneous materials, wind blown dust, as well as sample container material, are suspected problems prior to analysis. Preservation techniques are being evaluated in an ongoing study by Environment Canada (108).

Several future needs for a better understanding of the atmospheric transport of mercury can be identified:

- more extensive monitoring of ambient levels and deposition rates, utilizing techniques known to



provide meaningful results. Implicit in this requirement is the need for improved sampling techniques, particularly for precipitation sampling

- a more concerted effort to experimentally confirm the types of mercury compounds presumed to occur in the atmosphere and subsequently to identify important transformations (organomercury compounds to elemental mercury, for example)
- the effectiveness of precipitation washout as a deposition mechanism should be further evaluated and the probable significance of dry vapour deposition explored.

The work programme to be undertaken in subsequent phases of this study hopefully will fulfill several of these needs. Extensive measurements of ambient levels of mercury will be made using both a continuous real-time instrument and cumulative sampling techniques. Particulate, elemental and organic fractions will be identified. It is anticipated that improved precipitation sampling methods will be available for use in the study, and basic meteorological measurements will be available for interpretation of the results.

Two areas in which expansion of the planned work should be considered have been identified in the conduct of this review:

- assessment of the importance of local mantle degassing relative to long-range transport. The limited vertical profile studies contemplated in the original work programme may not prove adequate
- experimental and theoretical assessment of the deposition rate for dry vapour on fresh water possibly as a function of pH should be considered. No such studies are included in the present work programme but could prove to be extremely useful in delineating the mechanism whereby elevated mercury levels occur in the fish of remote lakes

in Ontario. It is, however, recognized that a completely separate study may be required to properly evaluate such a complex aspect of the mercury deposition mechanism.



N.D. Johnson,  
Assistant Research Scientist,  
Dept. of Environmental Chemistry.



J. Christison  
Senior Research Scientist,  
Pesticide & Trace Analytical Lab.  
Dept. of Applied Chemistry.



S.C. Barton,  
Vice President,  
United Technology & Science, Inc.,



J. Robbins,  
Head, Analytical  
Instrumentation Section,  
Scintrex Limited.

NDJ/SCB/JC/JR/yp  
October 5, 1978.

8. REFERENCES

1. L.J. Goldwater, Mercury in the Environment, Scientific American 224 (5), 15 (1971).
2. L. Friberg and Vostal, Mercury in the Environment, The Chemical Rubber Co., CRC Press, Cleveland, Ohio, 1972.
3. I.R. Jonasson, Mercury in the Natural Environment. A review of recent work, Geological Survey of Canada, Paper No.70-57 (1970).
4. Mercury in the Environment, Geological Survey, Professional Paper 713, U.S. Department of the Interior (1970).
5. Battelle Columbus Laboratories, Multimedia Levels - Mercury, prepared for U.S. Environmental Protection Agency, NTIS PB 273 201, September, 1977.
6. National Academy of Sciences, an Assessment of Mercury in the Environment, a Report prepared by the Panel on Mercury of the Coordinating Committee for Scientific and Technical Assessments of Environmental Pollutants, Environmental Studies Board, Commission on Natural Resources, National Research Council, Washington (1978).
7. L.M.Azzaria and F. Habashi, Mercury Pollution - An Examination of some Basic Issues, CIM Bulletin, 101, August 1976.
8. Environment Canada, National Inventory of Sources and Emissions of Asbestos, Beryllium, Lead, and Mercury. Summary of Emissions for 1970, Report EPS 3-AP-74-1, Air Pollution Control Directorate, January 1974.
9. Q.R. Stahl, Preliminary Air Pollution Survey of Mercury and its Compounds, a Literature Review, prepared for U.S. Department of Health, Education, and Welfare (1969).
10. C.T.Charlebois, An Overview of the Canadian Mercury Problem, Science Forum 10 (5), 17 (1977).
- 10a. F.M. D'Itri, Sources of Mercury in the Environment, International Conference on Environmental Mercury Contamination, Ann Arbor, Michigan, September 30, 1970.
11. R.J.P. Brouzes, R.A.N.McLean and G.H. Tomlinson, The Link between pH of Natural Waters and the Mercury Content of Fish, Paper presented at the Meeting of the U.S. National Academy of Sciences - National Research Council Panel on Mercury (1977).

12. D.H. Matheson, The Atmospheric Transport of Mercury - a Review of the Current Literature, Inland Waters Directorate, Canada Centre for Inland Waters (1977).
13. R.A.Rae, L.M.Reynolds and S.C.Barton, Ontario Research Foundation, A Study of Atmospheric Mercury Deposition in Ontario, Proposal No. P-2699/G, November 1977.
14. U.S.Environmental Protection Agency, Mercury and Air Pollution: a Bibliography with Abstracts, Publication No. AP-114, October 1972.
15. R.J. Brown, Mercury Pollution. Vol.1. 1974-1976. A Bibliography with Abstracts, NTIS PS-78/0479, May 1978.
16. R.J. Brown, Mercury Pollution. Vol.2. 1977 - April 1978. A Bibliography with Abstracts, NTIS PS-78/0480, May 1978.
17. D.B. Peakall and R.J. Lovett, Mercury: Its Occurrence and Effect in the Ecosystem, Bioscience 22 (1) 20 (1972).
18. J.R.Jonasson and R.W. Boyle, Geochemistry of Mercury, Paper presented at the Royal Society of Canada Symposium, Mercury in Marine Environment, Ottawa, February 15 and 16, 1971.
19. A.Katz and P.A. Krenkel, Mercury Pollution: the Making of an Environmental Crisis, CRC Critical Reviews in Environmental Control, 2 (4), 517 (1972).
20. W.H.Van Horn, Materials Balance and Technology Assessment of Mercury and its Compounds on National and Regional Bases, U.S. Environmental Protection Agency, NTIS PB 247 000, (1975).
21. J.G.Sherbin, Mercury in the Canadian Environment, Volumes I and II, Draft Report prepared by the Environmental Protection Service, Fisheries and Environment Canada, January 1978.
22. G.E.Bangay, Discussion Paper-Production and use of Mercury in Canada, Canada Centre for Inland Waters, Paper No. 71-8, (1971).
23. U.K. Department of the Environment, Environmental Mercury and Man, a Report of an Inter-Departmental Working Group on Heavy Metals, Department of the Environment, Central Pollution Paper No.10, H.M.S.O.(1976).
24. D.R. Miller and L. Lands, Atmospheric Transport of Mercury, Draft Report No. 2 prepared by the Monitoring Assessment Research Centre, London, August 1977.
25. E.L. Kothny, The Three-Phase Equilibrium of Mercury in Nature, Trace Elements in the Environment, Advances in Chemistry Series No. 123, American Chemical Society, 48 (1973).

26. Illinois Institute for Environmental Quality, A Model for establishing an ambient Air Standard for Mercury in the State of Illinois, I.I.E.Q. Document No. 76/06, June 1976.
27. Science Council of Canada, Policies and Poisons, the Containment of Long-Term Hazards to Human Health in the Environment and in the Workplace, Report No. 28, October 1977.
28. H.B.H. Cooper Jr., S.D. Rawlings and R.S. Foote, Air-Water-Land Interfaces of Mercury in Urban Atmospheres, American Institute of Chemical Engineers, A.I.Ch.E. Symposium, 71 (145) (1974).
29. M.Fleisher, Summary of the Literature on the Inorganic Geochemistry of Mercury, U.S. Geological Survey, Professional Paper No. 713 (1970).
30. E.M.Cameron and J.R. Jonasson, Mercury in the Precambrian Shales of the Canadian Shield, Geoch. Cosmochim. Acta 36, 985 (1972).
31. J.E. Robbins, Mercury Vapour Analysis using Field Portable Zeeman Equipment with emphasis on Application of the Method in the Cordillera, Paper presented at the 75th Annual General Meeting of CIMM, Vancouver (1973).
32. J. Kozuchowski and D.L. Johnson, Gaseous Emissions of Mercury from Aquatic Vascular Plants, Nature 274, 468 (1978).
33. D.D. Gay, L.C. Fortmann, K.O. Wirtz and C.W. Frank, Dimethylmercury: Volatilization from Plants, Paper presented at the Fourth Joint Conference on Sensing of Environmental Pollutants, New Orleans, November 6-11, 1977.
34. H.V. Weiss, M. Koide and E.D. Goldberg, Mercury in the Greenland Ice Sheet: Evidence of Recent Input by Man, Science 174, 692 (1971).
35. J.M. McNeal and A.W. Rose, The Geochemistry of Mercury in Sedimentary Rocks and Soils in Pennsylvania, Geochim.Cosmochim. Acta 38, 1739 (1974).
36. A. Eshelman, S.M. Siegel and B.Z. Siegel, Is Mercury from Hawaiian Volcanoes a Natural Source of Pollution?, Nature 233 (15), 471 (1971).
37. Siegel et al, Mercury Emissions in Hawaii: Aerometric Study of the Kalalua Eruption in 1977, Environmental Science and Technology 12 (9), 1036 (1978).
38. Environment Canada, Mercury Losses from Chlor-alkali Plants, Eco/Log Week, March 3, 1978.

39. G. Lovblad and P. Greenfelt, Heavy Metals and other Trace Elements in Black Coal and their Emission to the Air at Coal Combustion, NTIS IVL-B-345 (1977).
40. A.B. Crocket and R.R. Kinnison, Mercury Distribution in Soil around a Large Coal-Fired Power Plant, U.S. Environmental Protection Agency Report, NTIS PB-269 289 (1977).
41. J.H. Horton, R.S. Dorsett and R.E. Cooper, Trace Elements in the Terrestrial Environment of a Coal-Fired Powerhouse, Dupont Report No. DP-1475, September 1977.
42. O.I. Joensuu, Fossil Fuels as a Source of Mercury Pollution, Science 112, 1027 (1971).
43. D.H. Klein and A.W. Andren, Trace Element Discharges from Coal Combustion for Power Production, Water, Air and Soil Pollution 5 (1), 71 (1975).
44. C.E. Billings and W.R. Matson, Mercury Emissions from Coal Combustion, Science 176, 1232 (1972).
45. Oak Ridge National Laboratory, Trace Elements at the Coal-Fired Allen Steam Plant, ORNL Progress Report Feb. 1973 - July 1973, (1974).
46. R.S. Braman and D.L. Johnson, Selective Absorption Tubes and Emission Technique for Determination of Ambient Forms of Mercury in Air, Environmental Science and Technology 8 (12), 996 (1974).
47. E.A. Jenne, Atmospheric and Fluvial Transport of Mercury, U.S. Geological Survey, Professional Paper No. 713, 40 (1970).
48. S.H. Williston, Mercury in the Atmosphere, Journal of Geophysical Research, 73 (22), 7051 (1968).
49. W. Lockeretz, Deposition of Airborne Mercury near Point Sources, Water, Air and Soil Pollution 3, 179 (1974).
50. J.R. Jonasson and R.W. Boyle, Geochemistry of Mercury and Origins of Natural Contamination of the Environment, Canadian Mining and Metallurgy Bulletin 65 (717), 33 (1972).
51. B.Z. Siegel et al, Icelandic Geothermal Activity and the Mercury of the Greenland Icecap, Nature 241 (5391), 526 (1973).
52. B.P. Abramovskiy, et al, Global Balance and Maximum Permissible Mercury Emissions into the Atmosphere, Second Joint U.S./U.S.S.R. Symposium on the Comprehensive Analysis of the Environment, October 21-26, 1975, Honolulu (1975).

53. C. Eberling, W. Geins, J. Slemr and W. Sailer, A Method for Measurements of Mercury in the Atmosphere and some Results of the Global Hg - Distribution, Special Environmental Report No.10, World Meteorological Organization, WMO No. 460 (1976).
54. A. Hendriques, J. Isberg and D. Kjellgren, Collection and Separation of Metallic Mercury and Organo-Mercury Compounds in Air, *Chemica Scripta* 4, 139 (1973).
55. A.F. Jepson, Measurements of Mercury Vapour in the Atmosphere, Trace Elements in the Environment, *Advances in Chemical Series* No. 123, American Chemical Society, 48 (1973).
56. R. Dams and J. De Jonge, Chemical Composition of Swiss Aerosols from the Jungfrauoch, *Atmospheric Environment* 10, 1079 (1976).
57. K.K.S. Pillay, C.C. Thomas Jr., J.A. Sondel and C.H. Hyche, Mercury Pollution of Lake Erie Ecosphere, *Environmental Research* 5, 172 (1972).
58. E.P. Scheide, J.J. Filliben and J.K. Taylor, Survey of the Occurrence of Mercury, Lead and Cadmium in the Washington, D.C. Area, Presented at the American Chemical Society (1978).
59. P. Liroy, G. Wolff and T. Kneip, Toxic Airborne Elements in the New York Metropolitan Area, Presented at the APCA Toxic Air Contaminants: Their Measure, Evaluation and Control Conference, Newark, October 21, 1977.
60. A.W. Andren, Geochemical Cycling in a Watershed: Measurements of Atmospheric Input, *American Chemical Society, Division of Environmental Chemistry* 15 (2), 48 (1975).
61. U. Hogstrom, Wet Fallout of Sulfurous Pollutants Emitted from a City during Rain or Snow, *Atmospheric Environment* 8 (12), 129, (1974).
62. R.E. Jervis, J.J. Paciga and A. Chattopadhyay, Characterization of Urban Aerosols and their Hazard Assessment by Size Sampling combined with Inter Element Ratios, *International Symposium Atomic Energy Agency, Detection and Control of Environmental Pollutants*, Vienna, 1976, Detection and Control of Environmental Pollutants (1976).
63. N.J. Pattenden, Atmospheric Concentrations and Deposition Rates of some Trace Elements Measured in the Swansea/Neath/Port Talbot area, *Environmental and Medical Science Division, U.K.A.E.A. Research Group* (1974).
64. J.E. Evendijk, Trace Metal Content of Atmospheric Dust in Rotterdam, *Proceedings of the Fourth International Clean Air Congress, Tokyo*, May 16-20, 1977.



65. T. Wallin, Deposition of Airborne Mercury from Six Swedish Chlor-Alkali Plants Surveyed by Moss Analysis, Environmental Pollution 10, 101 (1976).
66. A.W. Andren and S.E. Lindberg, Atmospheric Input and Origin of Selected Elements in Walker Branch Watershed, Oak Ridge, Tennessee, Water, Air and Soil 8 (2), 201 (1977).
67. R.B. King, et al, Elemental Composition of Airborne Particulates and Source Identification: An Extensive One Year Survey, Journal of the Air Pollution Control Association 26 (11), 1073 (1976).
68. K.A. Rahn, The Chemical Composition of the Atmospheric Aerosol, University of Rhode Island, Technical Report, July 1, 1976.
69. W.L. Anderson and K.E. Smith, Dynamics of Mercury at a Coal-Fired Power Plant and adjacent Cooling Lake, Environmental Science and Technology 11 (1), 75 (1977).
70. H.A. Schroeder, Metals in Air, Environment 13 (8) (1971).
71. B.A. Soldano, P. Bien and P. Kwan, Air-Borne Organo-Mercury and Elemental Mercury Emissions with emphasis on Central Sewage Facilities, Atmospheric Environment 9, 941 (1975).
72. J.O. Ledbedder, B.A. Soldano, Discussion on Air-Borne Organo-Mercury and Elemental Mercury Emissions with emphasis on Central Sewage Facilities, Atmospheric Environment 10 (2), 171 (1976).
73. D.L. Johnson and R.S. Braman, Distribution of Atmospheric Mercury Species Near Ground, Environmental Science and Technology 8, 1003 (1974).
74. A. Hendriques and J. Isberg, New Method for Collection and Separation of Metallic Mercury and Organo-Mercury, Chemica Scripta 8, 173 (1973).
75. S.C. Barton, Heavy Metals in the Ontario Environment: an Overview, Unpublished Report Presented at the Air Pollution Control Association, Ontario Section Annual Spring Meeting, Toronto, April 20-24, 1975.
76. M.J. Bumbao, J.H. Shelton and D.A. Williams, Ambient Air Levels of Mercury in the Vicinity of Selected Chlor-Alkali Plants, Air Pollution Control Directorate, Report No. EPS 5-AP-73-12, July 1973.
77. J.C. Robbins, Mercury as a Geochemical Trace Element, Unpublished Memo, Scintrex Ltd., Concord, Ont. (1975).



78. W.P. Sears, Mercury in Base Metal and Gold Ores of the Province of Quebec, CIM Special Volume 11 (1971).
79. J.R. Jonasson and D.F. Sangster, Variations in the Mercury Content of Sphalerite from some Canadian Sulphide Deposits, Fifth International Symposium on Geochemical Explorations, Vancouver, April 1974.
80. J.R. Jonasson and R.J. Allen, Snow: A Sampling Medium in Hydrogeochemical Prospecting in Temperate and Permafrost Regions, Geochemical Exploration, IMM London (1972).
81. C. Brosset and I. Svedung, Preliminary Study of the Possibility of a Relationship between High Acidity in Lakes and High Mercury Content in their Fish Populations, Swedish Water and Air Pollution Research Lab., NTIS IVL-B-378, June 1977.
82. D.J. Pascoe, Joint Mercury Monitoring Program, Environmental Protection Service/Ontario Ministry of the Environment, MS Report No. OR-4, November, 1976.
83. A. Jerneloev and T. Wallin, Air-Borne Mercury Fall-Out on Snow around Five Swedish Chlor-Alkali Plants, Atmospheric Environment 7 (2), 209 (1973).
84. K. Matsumaga and S. Goto, Mercury in the Air and Precipitation, Geochemical Journal 10, 107 (1976).
85. K.E. Thrane, Background Levels in Air of Lead, Cadmium, Mercury and some Chlorinated Hydrocarbons measured in South Norway, Atmospheric Environment 12, 1155 (1978).
86. H.B. Cooper Jr., G.D. Rawlings and R.S. Foote, Measurement of Mercury Vapour Concentrations in Urban Atmospheres, Instrumental Society of America Trans. 13 (4), 296 (1974).
87. R.D.S. Stevens and R.J. Vet, Acidic Precipitation, Air Resources Branch, Ministry of the Environment, Province of Ontario (1978).
88. E.F. Muller and J.R. Kramer, Precipitation Scavenging in Central and Northern Ontario, ERDA Symposium Series No. 41, Precipitation Scavenging, Proceedings of a Symposium, Champaign, Illinois, CONF-741003-3 (1974).
89. J. Nordoe, Long Range Transport of Air Pollutants in Europe and Acid Precipitation in Norway, Water, Air and Soil Pollution 6, 199 (1976).
90. J.M. Lalancette, Pollution by Mercury, Recovery of Mercury from Polluted Water through Peat Treatment, University of Sherbrooke, Sherbrooke, Quebec (1971).

91. S.C. Fang, Sorption and Transformation of Mercury Vapour by Dry Soil, *Environmental Science and Technology* 12 (3), 285 (1978).
92. S. Chilov, Determination of Small Amounts of Mercury, *Talanta* 22, 205 (1975).
93. A.V. Holden, Mercury in Fish and Shellfish, *Journal of Food Technology* 8, 1 (1973).
94. R.S. Reimers, W. Dickinson Burrows and P.A. Krenkel, Total Mercury Analysis, *Critical Reviews in Environmental Control* Vol. 2, 343 (1973).
95. R.A. Wallace, W. Fulkerson, W.D. Shults and W.S. Lyon, Mercury in the Environment, The Human Element, ORNL-NSF-EPI, Oak Ridge National Laboratory, Oak Ridge, Tenn., March 1971.
96. A.M. Ure, The Determination of Mercury by Non-Flame Atomic Absorption and Fluorescence Spectrometry - A Review, *Anal. Chemica Acta* 76, 1 (1975).
97. D.C. Manning, Non-Flame Methods for Mercury Determination by Atomic Absorption - A Review, *Atomic Absorption Newsletter* 9, 97 (1970).
98. J.D. Brooks and W.E. Wolfram, Trace Mercury Determination, *American Laboratory* 3, 54 (1971).
99. J.R. Rhodes et al, Energy Dispersive X-Ray Fluorescence Analysis of Air Particulates in Texas, *Environmental Sciences and Technology* 6, 922 (1972).
100. P.R. Harrison, Areawide Trace Metal Concentrations Prepared by Multielement Neutron Activation Analysis, *Journal of the Air Pollution Control Association* 21, 563 (1971).
101. Brar, Thermal Neutron Activation Analysis of Particulate Matter in Surface Air of the Chicago Metropolitan Area, *Environmental Science and Technology* 4, 50 (1970).
102. S.C. Wroblewski, S.M. Spittler and P.H. Harrison, Mercury Concentration in the Atmosphere in Chicago, A New Ultra-sensitive Method employing Amalgamation, *Journal of the Air Pollution Control Association* 24 (8), 778 (1974).
103. E.E. Campbell, D.E. Trujillo and S.O. Wood, Development of a Multistage Tandem Air Sampler for Mercury, Los Alamos Scientific Laboratory, Quarterly Report No. LA-S 340-PR, (1973).
104. I.K. Iskander, J.K. Syers, L.W. Jacobs, D.R. Keeney and J.T. Gilmour, Determination of Total Mercury in Sediments and Soils, *Analyst* 97, 388 (1972).

105. H. Agemian and A.S.Y. Chau, An Improved Digestion Method for the Extraction of Mercury from Environmental Samples, *Analyst* 101, 91 (1976).
106. L.W. Jacobs and D.R. Keeney, Aqua Regia for Quantitative Recovery of Mercuric Sulphide from Sediments, *Environmental Science Technology* 8, 267 (1974).
107. W.R. Hatch and W.L. Ott, Determination of Submicrogram Quantities of Mercury by Atomic Absorption Spectrophotometry, *Analytical Chemistry* 40, 2085 (1968).
108. I.E.C. Contract, Feasibility Study on the Measurement of Atmospheric Mercury Deposition, Dept. of Supply and Services, Contract # OSS 77-00194, (1978).
109. J. Carron and H. Agemian, Preservation of Sub-ppb Levels of Mercury in Distilled and Natural Fresh Waters, *Anal. Chimica Acta* 92, 61 (1977).
110. K.I. Mahan and S.E. Mahan, Mercury Retention in Untreated Water Samples at the Part-per-billion Level, *Analytical Chemistry* 49, 662 (1977).
111. H.V. Weiss and W.H. Shipman, Effective Storage of Dilute Mercury Solutions in Polyethylene, *Anal.Chim. Acta* 81, 211 (1976).
112. J.M. Lo and C.M. Wei, Mercury Loss from Water during Storage Mechanisms and Prevention, *Analytical Chemistry* 47 (11), 1869 (1975).
113. C. Feldman, Preservation of Dilute Mercury Solutions, *Analytical Chemistry* 46, 99 (1974).
114. M. Stoeppler and W. Matthes, Storage Behaviour of Inorganic Mercury and Methylmercury Chloride in Sea Water, *Anal. Chimica Acta* 98, 389 (1978).
115. L. Kopp, M.C. Longbottom and L.B. Lobring, Cold Vapour Method for determining Mercury, *Journal of American Water Works Association* 64, 20 (1972).
116. J.L. Monkman, P.A. Maffett, T.E. Doherty, Determination of Mercury in Air Samples and Biological Material, *Industrial Hygiene Association Quarterly* 17, 418 (1956).
117. R.G. Drew and E. King, Determination of Atmospheric Mercury Trapped in Permanganate Solutions, *Analyst* 82, 461 (1957).
118. A.L. Lynch, R.F. Stalzer and D.T. Lefferts, Methyl and Ethyl Mercury Compounds - Recovery from Air and Analysis, *American Industrial Hygiene Association Journal* 29, 77 (1968).

119. D. Gardner, Rapid Method for Determination of Mercury in Air by Flameless Atomic Absorption, *Anal. Chemica Acta* 82, 321 (1976).
120. Air Pollution Control Directorate, Standard Reference Methods for Source Testing; Measurement of Emissions of Mercury from Mercury cell Chlor-alkali Plants, Fisheries and Environment Canada, EPS Report No. 1-AP-76-1, November 1976.
121. Y. Kimura and V.L. Miller, Vapour Phase Separation of Methyl or Ethylmercury Compounds, *Anal. Chemica Acta* 27, 325 (1962).
122. W.E. Makris, The Comparison of Five Published Methods for the determination of Mercury in Air, Paper presented at the Fourth Joint Conference on Sensing of Environmental Pollutants, New Orleans, November 6-11, 1977.
123. J.N. Driscoll, Sampling and Analytical Techniques for Measuring Mercury in Stationary Sources. State-of-the-art-report, *Health Lab. Science* 11 (4), 348 (1974).
124. A.E. Moffit and R.E. Kupel, A Rapid Method employing Impregnated Charcoal and Atomic Absorption Spectrophotometry for the determination of Mercury, *Journal American Industrial Hygiene Association* 32, 614 (1971).
125. C.M. Christian and J.W. Robinson, Direct Determination of Cadmium and Mercury in the Atmosphere, *Anal. Chemica Acta* 56, 466 (1971).
126. A.O. Rathje, D.H. Marcero and D. Dattilo, Personal Monitoring Technique for Mercury Vapour in Air and determination by Flameless Atomic Absorption, *American Industrial Hygiene Association Journal* 35, 571 (1974).
127. T.Y. Soribara and C.F. Shield, The Analyses of Submicrogram Amounts of Mercury in Tissues, *Journal American Industrial Hygiene Association* 29, 87 (1968).
128. E.G. Pappas and L.A. Rosenberg, Determination of Submicrogram Quantities of Mercury by Cold Vapour Atomic Absorption Photometry, *ibid* 49, 782 (1966).
129. A.A. Christie, A.J. Dunson and B.S. Marshall, Field Methods for Determining Certain Organomercurial Vapours in Air, *Analyst* 92, 185 (1967).
130. J.H. Janssen, J.E. Van Den Enk, R. Bult and D.C. De Groot, Determination of Total Mercury in Air by Atomic Absorption Spectrophotometry after collection on Manganese Dioxide, *Anal. Chemica Acta* 92, 71 (1977).

131. H. Brandenberger and H. Bader, Determination of Nanogram Levels of Mercury in Solution by Flameless Atomic Absorption Technique, *Helvetica Chimica Acta* 50, 1409 (1967).
132. D. Dattilo, D.H. Marcero and A.O. Rathje, Personal Monitoring Technique for Mercury Vapour in Air and Determination by Flameless Atomic Absorption, *Journal American Industrial Hygiene Association* 35 (9), 571 (1974).
133. H.A. Van der Sloot, Determination of Mercury in Air by Neutron Activation Analysis, *Analytica Chimica Acta* 70, 439 (1974).
134. R. Goldberg, S.L. Guinivan and R.M. Tuggle, Field Testing the Scaringelli and Thompson Ambient Mercury Methods, *Air Pollution Control Association: 68th Annual Meeting and Exhibition*, 272 (1975).
135. F.P. Scaringelli and R.J. Thompson, Determination of Total Mercury in Air by Charcoal adsorption and Ultraviolet Spectrophotometry, Paper presented at American Chemical Society, National 165th Meeting, Dallas, Texas (1973).
136. G. Thilliez, Rapid and Accurate Determination of Traces of Mercury in Air and in Biological Media by Atomic Absorption, *Chemic. Analyt* 50, 226 (1968).
137. W.W. Vaughn and J.H. McCarthey Jr., An Instrument Technique for Determination of Submicrogram Concentrations of Mercury in Soils, Rocks and Gas, *U.S. Geological Survey Professional Paper* 501D, D123 (1964).
138. L.M. Azzaria and G.R. Debbier, Mercury Analysis in Geochemical Exploration, *Bull. Can. Mining and Metal* 62, 521 (1969).
139. O.I. Joensuu, Mercury-Vapour Detector, *Applied Spectroscopy* 25, 526 (1971).
140. J.V. O'Gorman, N.H. Suhr and P.L. Walker, Determination of Mercury in some American Coals, *Applied Spectroscopy* 26, 44 (1972).
141. C.M. Baldeck, G.W. Kalb and H.L. Crist, Determination of Elemental mercury in an emission source having high sulphur dioxide concentration by Amalgamation with Gold and Ultraviolet Spectrophotometry, *Analytical Chemistry* 46, 1500 (1974).
142. A.M. Hartley and D.J. Devine, A Method for the determination of Total Mercury in Ambient Air, *Illinois Institute for Environmental Quality*, NTIS PB 255 698 (1976).
143. W.W. Vaughn, A Simple Mercury Vapour Detector for Geochemical Prospecting, *U.S. Geological Survey, Circ.* 540, 8pp (1967).

144. J. Scullman and G. Widmark, Collection and Determination of Mercury in Air, *International Journal of Environmental and Analytical Chemistry* 2, 29 (1972).
145. Z.G. Bell, M.W. Wood and L.A. Kuryia, Mercury Exposure Evaluations and their Correlation with Urine Mercury Excretions I. Method to determine Mercury Time Weighted Average Exposures, *Journal of Metals* 15, 340 (1973).
146. G.L. Corte, L. Dubois and J.L. Monkman, A Reference Method for Mercury in Air, *The Science of the Total Environment* 2, 89 (1973).
147. G.L. Corte, R.S. Thomas, L. Dubois and J.L. Monkman, Calibration Parameters for the Integrated Silver Method for Mercury in Air, *Science of the Total Environment* 2, 251 (1973).
148. G.L. Corte and L. Dubois, Determination of Trace Amounts of Mercury in Rock Samples, *Mikrochemica Acta* I, 69 (1975).
149. T.J. Kneip et al, Tentative Method of Analysis for Elemental Mercury in ambient Air by Collection on Silver Wool and Atomic absorption Spectroscopy, *Health Laboratory Science* 11 (4), 342 (1974).
150. S.J. Long, D.R. Scott and R.J. Thompson, Atomic absorption determination of Elemental Mercury collected from Ambient Air on Silver Wool, *Analytical Chemistry* 45 (13), 2227 (1973).
151. NIOSH Manual of Analytical Methods, Mercury in Air, U.S. Department of Health Education and Welfare, 175-1 (1974).
152. G.W. Kalb and C. Baldeck, The adaptation of the Gold Amalgamation Sampling and Analytical Procedure for the Analysis of Mercury in Stack Gases in high SO<sub>2</sub> Environments observed in Smelters, U.S. Department of Commerce, NTIS PB 211 215 (1972).
153. E.C. Amerod and R.P.W. Scott, Gas Chromatography of Polar Compounds using a Non-polar Liquid Phase, *Journal of Chromatography* 2, 65 (1959).
154. R. Robbins, Private Communication.
155. L.M. Azzaria, Mercury in Soil and Air as a Guide to Mineralization in Four Areas of Quebec, Department of Natural Resources, Special Publication S-136 (1973).
156. Q. Bristow, An Evaluation of the Quartz Crystal Microbalance as a Mercury Vapour Sensor for Soil, Gases, Geochemical Exploration Vol. 1, 55 (1972).



157. J.McNerney and P.R. Biseck, Geochemical Exploration using Mercury Vapour, Econ. Geol. Vol. 68, 1313 (1973).
158. J.C. Robbins, Zeeman Spectrometer for Measurement of Atmospheric Mercury Vapour, Geochemical Exploration, 315 (1972).
159. P.A. Krenkel, Mercury: Environmental Considerations, Part II, CRC Critical Reviews in Environmental Control 4 (3), 303 (1974).
160. O. Therkelsen, Environmental Mercury Pollution and Control, Vatten 33 (3), 299 (1977).
161. W. Stopford and L.J. Goldwater, Methylmercury in the Environment: A Review of Current Understanding, Environmental Health Perspectives 12, 115 (1975).
162. J.G. Calvert and J.N. Pitts, Photochemistry, J. Wiley and Sons, New York (1966).
163. R.R. Draxler and W.P. Elliott, Long Range Travel of Airborne Material subjected to Dry Deposition, Atmospheric Environment 11, 35 (1977).
164. A.W. Hogan, V.A. Mohnen and V.S. Schaefer, Comments on Oceanic Aerosol Levels deduced from Measurements of the Electrical Conductivity of the Atmosphere, Journal of Atmospheric Science 30, 1455 (1973).
165. W.P. Elliott, F.L. Ramsey and R. Johnston, Particle Concentrations over the Oceans, J. Rech Atmospher 8, 939 (1974).
166. J.W. Horst, A Surface depletion Model for deposition from a Gaussian Plume - A comparison of Surface and Source Depletion Models, Atmospheric Environment 11, 41 (1977).
167. D.G. Fox, Modelling atmospheric effects - an Assessment of the Problems, Proceedings of the 1st International Symposium on Acid Precipitation and the Forest Ecosystem, 12-15 May 1975, Columbus, 381 (1975).
168. L. Prahm et al, Long Range Transmission of Pollutants simulated by a Two Dimensional Pseudospectral Dispersion Model, Journal of Applied Meteorology 16 (9), 896 (1977).
169. D.G. Fox, Modelling Atmospheric Effects - an Assessment of the Problems, Water, Air, Soil Pollution 6 (2-3-4), 173 (1976).
170. L.L. Wendel et al, A Regional Scale Model for Computing Deposition and Ground Level Air Concentration of Sulfur Dioxide and Sulfates from Elevated and Ground Sources. Proceedings from the 3rd Symposium on Atmospheric Turbulence, Diffusion and Air Quality, 318 (1976).

171. F.B. Hill et al, Development of a Technique for the Measurement of Biogenic Sulphur Emission Fluxes, NTIS Publication No. BNL 23063.
172. R.G. Delumyea and R.L. Petel, Atmospheric Inputs of Phosphorus to Southern Lake Huron, April - October 1975, U.S. Environmental Protection Agency, NTIS PB 267 943 (1977).
173. T.A. McMahon, P.J. Denison and R. Fleming, A Long Distance Air Pollution Transportation Model incorporating Washout and Dry Deposition Component, Atmospheric Environment 10, 751 (1976).
174. F.B.Hill et al, A Model for Rain Composition and the Washout of Sulphur Dioxide, Atmospheric Environment 11 (10), 917 (1977).
175. H.L. Windom and R.A. Duce, Marine Pollutant Transfer, Lexington Books, D.C. Heath and Company, Lexington, Mass. (1976).
176. J.G. Droppo, D.W. Glover, A.B. Abbey, C.W. Spicer and J. Cooper, Measurement of Dry Deposition of Fossil Fuel Plant Pollutants, U.S. Environmental Protection Agency, NTIS PB-264 495 (1976).
177. J.A. Lodge, An Estimate of Deposition Velocities over Water, Atmospheric Environment 12, 973 (1978).
178. H. Sievering et al, Aerosol Deposition and Loading of Lake Michigan, Presented at the Fourth Joint Conference on Sensing of Environmental Pollutants, New Orleans 856, November 6-11, 1977.
179. J. Sadmor, M. Rindsberger and I. Zur, Deposition and Resuspension of Pollutants from and into the Atmosphere, Presented at the Fourth International Clean Air Congress, Tokyo 280, May 16-20, 1977.
180. J.A. Garland, The Dry Deposition of Sulfur Dioxide to Land and Water Surfaces, Presented at the Royal Society of London, Series A 354 (1678), 245 (1977).
181. H. Appelquist, K.O. Jensen and Torben Sevel, Mercury in the Greenland Ice Sheet, Nature 273 (22), 657 (1978).
182. H.V. Weiss, M.M. Herron and C.C. Langway Jr., Natural Enrichment of Elements in Snow, Nature 274 (27), 352 (1978).
183. P. Korringa and P. Hagel Jr., Proceedings of the International Symposium on the Problems of Contamination of Man and His Environment by Mercury and Cadmium, 3-5 July 1973, Luxembourg (1974).
184. R. Wollast, G. Billen and F.T. Mackenzie, Behaviour of Mercury in Natural Systems and its Global Cycle. Ecological Toxicology Research: Effects of Heavy Metal and Organohalogen Compounds. Proceedings of a NATO Science Committee Conference, edited by A.D. McIntyre and C.F. Mills. New York and London: Plenum Press. pp. 145-166 (1975).



185. E.G. Walther, Predicting the Transport of Air Pollutants from the Navajo and Kaiparowits Generating Stations in Lake Powell, Charles F. Kettering Foundation, Dayton, Ohio, 502 (1976).

APPENDIX I

An Annotated Bibliography On  
The Geochemistry of Mercury

This appendix is concerned with mercury geochemistry in the natural environment. The subject is divided into the following headings:

1. Normal abundances in the lithosphere
2. Abnormal concentrations in the lithosphere
  - (a) Deposits in which mercury minerals are predominant
  - (b) Mineral deposits in which mercury is an important trace or minor component
3. Ore forming processes
4. Dispersion processes
5. Bibliography

#### 1. NORMAL ABUNDANCES IN THE LITHOSPHERE

Fleischer (1970) (1)

Data on mercury in a variety of geological and environmental samples are presented. Many of the results presented here may not be very reliable since the analytical techniques that are sufficiently sensitive to measure the minute amounts of mercury involved have been perfected only fairly recently.

Average concentration of "continental rocks" is about 80 ppb, igneous rocks being rather lower (1 - 100 ppb) and sedimentary rocks rather higher (10 - 500 ppb).

Jonasson and Boyle (1972) (2)

Using essentially the same data base, a resume of worldwide data is again presented. Mechanisms for dispersal and concentration of mercury in the biosphere are discussed.

Department of the Environment (1976) (3)

A more recent set of data on mercury concentrations in a wide variety of geological and environmental samples is reported. Again, some of the results must be regarded as suspect, i.e. McCarthy's results for mercury in air sampled above base-metal deposits are now not regarded as valid.

Cameron and Jonasson (1972) (4)

Data was presented from 800 samples of Precambrian shales in Canada. Samples of Archean age of mainly volcanogenic origin, weakly metamorphosed, average 129 ppb Hg. Shales from a later era in the Precambrian, the Aphebian era which, in general, were of non-volcanogenic origin and variably metamorphosed had a much higher average mercury content of 513 ppb. It was suggested that "this enrichment of mercury in early Proterozoic sediments was related to increased rates of degassing of Hg from the earth caused by a change in the sites of magma generation from shallow depths in the oceanic crust and mantle to deeper levels in the mantle".

Much lower Hg levels were found in Paleozoic shales (average 42 ppb) from eastern Canada.

Garrett (1974) (5)

Mercury values from granitoid rocks of the Yukon were found to have extremely low levels with geometric means of 3-18 ppb, the higher levels being found in plutons associated with tungsten mineralization.

McNeal et al (1974) (6)

Problems in analytical chemistry of mercury, unreliability of mercury data, poor interlaboratory comparisons and heterogeneous nature of the USGS standard rocks are discussed.

## 2. ABNORMAL CONCENTRATIONS IN THE LITHOSPHERE

Anomalous Hg concentrations are associated with present-day tectonic activity. Mercury is, for instance, enriched in sediments located close to the East Pacific Rise. High levels in the volcanic gases and in the nearby atmosphere on the volcanic islands near Iceland that straddle the Mid-Atlantic ridge also have been recorded. Mercury is closely associated with the geothermal resources of the Geysers, California and Lardarello, Italy.

Mercury ore deposits represent the most favorable geological conditions for the concentrations of the metal for its normally extremely

low natural abundance.

(a) Deposits in which mercury minerals are predominant.

Fedorchuk (1974) (7); Ozerova and Vinogradov (1974) (8)

The geological settings of a wide variety of types of Hg deposits are reviewed. Commercial Hg deposits are concentrated along clearly traced linear structures, forming orebearing zones and belts up to 800 - 1000 km long. In tectonomagmatic respect the latter fall into three groups 1) those related to deep (marginal) faults which separate folded areas and zones of different facies environment; 2) belts localized along belts developed over peripheral parts of old stable massifs; 3) belts closer to faults which control present day or Alpine eruptive manifestations.

Mercury is not genetically associated with any definite type of magmatic rocks. Evidently it emanated as a degassing product along deep fault zones during their activation.

Bailey et al (1974) (9)

The uses of mercury, its production and the geology of mercury deposits were reviewed. Cinnabar (mercuric sulphide) is the major ore mineral and is found at comparatively shallow depths. "Because the deposits were formed near the surface in orogenic belts, it is likely that any geologically-ancient deposits have been eroded away. All deposits that can be accurately dated are Pliocene or younger. Comparison of the occurrence of Hg deposits with the new global elements (of the global tectonic theory) shows that most deposits occur on the continent-ward side of the post-Jurassic subduction zones. This suggests that Hg originally contained in the marginal eugeosynclinal sediments or perhaps in oceanic crustal materials has been distilled out of the downward-plunging plate and emplaced at a higher, cooler level along or above the subduction zone".

Moiseyev (1971) (10)

The amount of mercury liberated from sediments was estimated by numerical application of heat transfer theory to a geological model. Results suggested that quantities of mercury sufficient to form ore deposits would be generated without resorting to 'magmatic' origins.

Although cinnabar has historically been the major economic ore mineral, there are an immense variety of mercury minerals that occur extremely rarely. Two of these, however, have been found in economic quantities.

Tunnell (1976) (11)

The occurrence and conditions for formation of livingstonite, a mixed mercury/antimony sulphide, at Huitzuco, Mexico are reviewed.

Foord et al (1974) (12)

Corderoite ( $\alpha$ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ ) is recovered at what is presently probably the only major U.S. operating mercury mine. Corderoite is believed to have been formed from underlying primary cinnebar as a low-temperature sugergene mineral in Tertiary lake sediments.

Radtke et al (1972) (13)

The occurrence at the Carlin gold deposit, Nevada, of trace cinnabar associated with carbonaceous material, pyrite surfaces and as disseminated sulphide is described.

Hutchinson (1971) (14)

The similarity is suggested in volcanogenic origin of the tertiary gold deposits of Nevada and elsewhere with some of the Archean gold deposits in the Noranda-Larder Lake area. If, however, mercury was present in these more ancient deposits, it has been largely dispersed by subsequent tectonic and metamorphic events.

Smaller amounts of metallic mercury are usually found in the upper levels of mercury deposits.

- (b) Mineral deposits in which mercury is an important trace or minor component.

Where different sulphides co-exist, mercury is usually preferentially enriched in sphalerite, rather than, say, pyrite, chalcopyrite, galena, etc. The concentration of mercury in sulphides varies with the age and geological setting of the ore deposit. Zinc-bearing volcanogenic deposits, especially those of Proterozoic and Paleozoic age, often control high Hg

concentrations ( $n \times 10^2$  -  $N \times 10^3$  ppm). Zinc deposits that show little evidence of volcanic affiliation and are probably formed by the circulation of warm brine solutions (e.g. Stanton, 1972) usually have very low Hg levels ( $n \times 10$  -  $n \times 100$  ppb).

Jonasson and Sangster (1974)

Mercury levels in sphalerite from a number of Canadian deposits are tabulated. For deposits in Ontario, values ranged from very much less than 1 ppm in sphalerite from minor zinc showings in southwest Ontario to 161 ppm at the Errington mine in the Sudbury area.

Sears (1971)(16)

The distribution of mercury in selected base metal and gold deposits in the province of Quebec was studied. Analysis demonstrated that mercury is more abundant in zinc sulphide ores than in iron, copper or lead sulphides.

Jonasson and Allen (1972) (17)

A mercury prospect is known at Clyde Forks, Eastern Ontario. The mineralization consists of narrow veinlets and blobs of disseminated tetrahedrite, chalcopyrite and pyrite in barite-calcite gangue. Traces of cinnabar are visible in association with each of the sulphides. The tetrahedrite contains up to 4% mercury.

### 3. ORE FORMING PROCESSES

The formation of economic mercury deposits implies a concentrating factor of some  $10^4$  over crustal abundances. The composition and conditions required of "mineralizing fluids" that could produce such concentrations have been studied for many years, revolving around the problem of the extreme insolubility of mercuric sulphide in aqueous systems.

Krauskopf (1951) (18), White (1955) (19), Tunell (1964) (20)

These authors tackled the problem of mercury transport in hydrothermal fluids in various forms. "If the mercuric sulphide in liquid ore-

forming solutions was carried chiefly in the form of an alkaline sulphide complex. precipitation of cinnabar and/or metacinnabar was probably caused by falling temperature, by reduction of alkalinity resulting from reaction with wallrocks, and/or by admixture with less alkaline or acid groundwater". Objections were raised by White against the hypothesis that mercury sulphide was transported to the sites of mercury ore deposits as an alkali sulphide complex. The thermal waters most closely related to mercury deposits are near neutral rather than strongly alkaline. Krauskopf considered the transport of mercury in the vapour phase at elevated temperatures as being a significant factor in moving the quantities required.

Nriagu and Anderson (1970) (21)

The calculated solubilities of a number of sulphides including mercury sulphide in concentrated brine solutions containing the geologically pertinent ligands ( $\text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{HS}^-$ ,  $\text{H}_2\text{S}$ ) were presented.

Although chloride complexing was considered responsible for the large solubility of cadmium and lead sulphides it was unlikely that significant geochemical migration of mercury and copper at moderately low temperatures could have occurred. It seems possible however, that chloride complexing could have moved sufficient mercury to account for the very high levels of mercury found in some base metal sulphide deposits.

Learned et al (1974) (22)

The common occurrence of cinnabar and stibnite in well defined districts in the same epithermal environments suggested that similar physico-chemical processes are responsible for the genesis of the two minerals; however, cinnabar and stibnite tend to be segregated within these districts and also within individual deposits that contain both minerals. The solubilities of cinnabar and stibnite in aqueous  $\text{Na}_2\text{S}$  solutions that were simultaneously saturated were measured.

Watling et al (1972) (23)

Sulphide mineralization occurs at Keel, Eire. Mercuric sulphide was found to be concentrated in the vicinity of the base metal sulphides and mercuric chloride, however, was the predominant phase in rocks more



remote from sulphide ore.

"Data suggest that waters charged with metals in the form of chlorides and chloride-complexes migrated towards faults. The faulted area was an area of increased sulphur activity and temperature and consequently when the chloride-rich waters encountered the faulted region base metal sulphides were precipitated".

#### 4. DISPERSION PROCESSES

There has been keen interest over the last fifteen years in the possibility of, and the mechanisms for, release of mercury from base and precious metal deposits in the potential application of mercury measurements to mineral exploration. Despite this interest, very few theoretical or quantitative data have emerged but rather a mass of empirical and not always reliable field results. The presence of mercury vapour over cinnabar deposits is presumably due to the oxidation of the sulphide.

Karasik and Gerasimova (1967) (24)

The vapour pressure of mercury developed over cinnabar at various temperatures and under various conditions was determined both in the field and laboratory.

The release of mercury from other sulphides of varying mercury content is more problematical, particularly, those sulphides that are supposed to lie below a water table or zone of oxidation.

Jonasson and Boyle (1972) (2)

The generation of elemental Hg from a mercuriferous sulphides was suggested to occur as the reduction of mercury ions by electrons released due to the oxidation of the major sulphide ions present.

McNerney and Buseck (1973) (25)

Mechanisms for release of Hg from sulphides below the zone of oxidation were quoted. Polyvalent ions or non-stoichiometric phases provide possible sources. Changes of valency state in say, iron, would produce electrons to reduce mercuric ion. Sulphides of non-stoichiometric composition could also reduce  $\text{Hg}^{2+}$  as these ores changed towards

stoichiometry over geological time.

Trace metallic Hg could also be chemisorbed on crystal surfaces to be released by changes in either temperature or electrochemical potentials. Tectonic disturbances resulting in fracturing of crystals could also release mercury.

Razenkova et al (1972) (26)

Using a "chemical phase" method of analysis of the form of mercury in various oil horizons over a mercury deposit was determined. Soluble mercury (organometallic Hg and mercuric chloride), mercury sulphate, mercury oxides and oxychlorides, mercurous chloride, metallic mercury and mercuric sulphide were the components determined.

Robins (1975) (27)

Numerous case histories showing the existence of anomalous quantities of mercury over a variety of base and precious metal deposits, geothermal resources were presented. The results are similar to those found by many other workers applying mercury measurements to mineral exploration.

Significant reconcentrations of mercury after release from mercuriferous ores appear to have occurred very rarely. Mercury will be concentrated in carbonaceous material, which after diagenesis and varying degrees of metamorphism, may result in the higher levels seen in some shales (i.e. Cameron and Jonasson (1972)). These values are rarely more than 1 ppm.

van de Poll and Sutherland (1976) (28)

Schachnerite, a natural alloy of silver and mercury was found at the centre of "reduction spheres", spherical mineralized concentrations 1-6 centimetres in diameter, found in sedimentary rocks in New Brunswick. No mechanism for the extreme concentration of mercury into this mineral was presented.

The conversion of inorganic forms of mercury to various organic species and their consequent fate in the biosphere has received much attention, especially in the literature concerned with mercury pollution.

This aspect is not covered here. Reverse process, i.e. the release of elemental mercury, either from organic materials or by the action of organic materials on inorganic mercury, has also been recently reported.

Alberts et al (1974) (29)

Elemental Hg is formed in aqueous solution by the chemical reduction of mercuric ion in the presence of humic acid. 'The reaction mechanism involves interaction of the ionic metal species with the free radical electrons of the humic acid'.

Spangler et al (1973) (30)

Methylmercuric ion is converted to elemental mercury in lake sediments in the presence of micro-organisms with subsequent loss of the volatile  $\text{Hg}^0$ .

Kozuchowski and Johnson (1978) (31)

A significant release of Hg was shown by plants growing on the shoreline of a lake known to be contaminated with mercury. Tests for the presence of organo-mercurels were negative. The authors concluded 'vascular plants may play an important part in the removal of mercury from soils and sediments by injecting it directly into the atmosphere'.

Mercury emitted to the atmosphere is eventually returned to the surface by rains, thus completing the geochemical cycle.

Robbins (1973) (32)

Rain very readily washes mercury from the atmosphere. Sufficient rainfall will also cause significant variations in mercury levels of the atmospheric gases trapped in soils. From data taken in Tasmania, it may take several days after heavy rain for mercury levels to return to their former equilibrium levels.

McNeal & Rose, (1974) (33); Weiss et al (1971) (34)

These authors produced geochemical budgets that related the exhalation of mercury from the lithosphere, the mean residence time of mercury in the atmosphere as indicated by the frequency of rainfall, the level of mercury in rainwater and the levels of mercury in soil or sedimentary rocks. The data on rates of mercury exhalation and on the

levels in rainwater seem to be so sparse that the general validity of such a mercury geochemical budget is hard to justify.

BIBLIOGRAPHY

1. Fleischer, M. (1970), Summary of the literature in the inorganic geochemistry of mercury, U.S. Geological Survey Professional Paper 713.
2. Jonasson, I.R., and Boyle, R.W. (1972), Geochemistry of mercury and origin of Natural contamination of the environment, CIM Bull. Vol. 65, No. 717, pp 32-39.
3. Department of the Environment (1976), Environmental mercury and man. Pollution Paper No. 10, HMSO London.
4. Cameron, E.M. and Jonasson, I.R. (1972) Mercury in precambrian shales of the Canadian shield, Geochemistry Cosmochim Acta Vol. 36, pp 985-1005.
5. Garrett, R.G. (1974), Mercury in some granitoid rocks of the Yukon and its relocation to gold tungsten mineral Geochemistry Expl. Vol. 3, pp 277-290.
6. McNeal, J.M. (1974), Trace element mode of occurrence in stream sediment, GSA Abstracts Vol. 6, No. 7, p866.
7. Fedorchuk, V.P. (1974), Genetic and commercial types of mercury deposits, 1 Congreso Internacional del Mercurio, Barcelona, 6-10 May.
8. Ozevo, N.A. and Vinogradov V.E. Certain aspects of the genesis of mercury deposits, 1 Congreso Internacional del Mercurio, Barcelona, 6 - 10 May.
9. Bailey, E.H., Clark, A.L., and Smith, R.M. (1974), Mercury in U.S. Geol. Survey Prof. Paper 820.
10. Moiseyev, A.N., (1971) A non-magmatic origin for mercury ore deposits, Econ. Geol. Vol. 66, pp 591 - 601.
11. Tunell, G. et al (1976) On the origins of livingstonite at Huitzuco, Guerrero, Mexico, Min. Depos. Vol. 11, pp 71 - 82.
12. Foord, E.E., Berendson, P, and Storey, L.O. (1974) Corderoite, first natural occurrence of  $x - \text{Hg}_3\text{S}_2\text{Cl}_2$  from the Cordero Mercury Deposit Humboldt County, Nevada, Amer. Miner. Vol. 59 pp 652 - 655.

13. Radtke, A.S. and Taylor, C.M. and Christ, C.L. (1972), Chemical distribution of gold and mercury at the Corlin deposit Econ. Geol. Vol. 67, p 1009.
14. Hutchison, R.W. Riddles, R.H., and Saffel, G.G. (1971) Metallogenic relationships in the Abitibi belt, Canada. A model for Archean metallogeny CIM Bull. Vol. 64 No. 708, pp 48 - 57.
15. Jonasson, R. and Sangster, D.F. (1974), Variations in the mercury content of sphalerite from some Canadian sulphide deposits. 5th International Symposium on Geochem. Expl. Vancouver, April.
16. Sears, W.P. (1971) Mercury in base metal and gold ores of the province of Quebec, CIM Spec. Vol. No. 11.
17. Jonasson, I.R. and Allen R.J. (1972), Snow: a sampling medium in hydrogeochemical prospecting in temperate and permafrost regions in Geochemical Exploration 1972 ed. Jones, M.J. London.
18. Krauskopf, K.B. (1951) Physical chemistry of quicksilver transportation in vien fluids. Econ. Geol. V.46, p498 - 523.
19. White, D.E. (1955), Thermal springs and epithermal ore deposits Econ. Geol. 50th Anniversary.
20. Tunell, G. (1964), Chemical processes for the formation of mercury ores and ores of mercury and antimony. Geol. Cosmoch. Acta. Vol. 28 pp 1019 - 1037.
21. Nriagu, J.O. and Anderson, G.M.L. (1970) Calculated solubilities of some base metal sulphides in brine solutions. Trans. IMM B708-212.
22. Learned, R.E. Runell, G. and Dickson, R.W. Equilibria of cinnebar, stibnite and saturated solutions in the system  $\text{HgS-Sb}_2\text{S}_3\text{-Ag}_2\text{S-H}_2\text{O}$  from  $150^\circ$  to  $250^\circ\text{C}$  at 100 bars with implications concerning ore genesis. Jour. Res. USGS Vol. 2. pp 457 - 466.
23. Watling, R.J. et al (1973) Trace identification of mercury compounds as a guide to sulphide mineralization at Keele, Eire in Geochem. Exp. 1972 and Jones, M.J. IMM London, pp 59 - 69.
24. Karasik, M.A. and Gerasimova, H. (1967) The conditions for mercury vapour formation over cinnebar Dokl. Accd. Sci. USSR (AGI publ.) V173, pp 199-201.

25. McNerney, J.J. and Buseck, P.R. (1973) Geochemical Exploration using mercury vapour Econ. Geol. Vol. 68, pp 1313 - 1320.
26. Razenkova, H.I. et al (1973) Forms of mercury in primary and secondary geochemical dispersion halos of the West Polar deposit Magaden Oblast. trams in Dokl. Akad. Nauk SSSR (AGI Publ.) Vol. 213, pp 209 - 211.
27. Robbins, J.C. 1975, Mercury as a geochemical trace element unpublished memo, Scintrex Limited, Concord, Ontario.
28. van der Poll, H.W. and Sutherland, J.K. (1976) Cupritiferous reduction spheres in Upper Mississippian redbeds of the Hopewell group at Dorchester Cape, New Brunswick, Can. Journ. Earth Sci. Vol. 13, pp 781 - 790.
29. Alberts, J.J. et al (1974), Elemental mercury evolution mediated by humic acid. Science Vol. 184 (May) pp 895 - 896.
30. Spangler, W.J. (1973) Methylmercury bacterial degradation in lake sediments, Science Vol. 180, p 192.
31. Kozuchowski, J. and Johnson, A.L. (1978) Gaseous emissions of mercury from an aquatic vascular plant, Nature Vol. 274, pp 468 - 469.
32. Robbins, J.E. (1973) Mercury vapour analyses using field Zeeman equipment with emphasis on application of the method the Cordillera paper presented at the 75th Annual General Meeting of CIMM, Vancouver.
33. McNeal, J.M. and Rose, A.W. (1974) The geochemistry of mercury in sedimentary rocks and soils in Pennsylvania, Geoch. Cosmoch. Acta Vol. 38, pp 1759 - 1784.
34. Weiss, H.V. et al (1971) Mercury in a Greenland ice sheet: evidence of recent input by man. Science Vol. 174 (November) pp 692 - 694.

APPENDIX II

Contractor's Terms of Reference for the Study to Determine Atmospheric  
Mercury Deposition

Preamble:

Mercury and its compounds appear in all environmental media as a result of both natural and anthropogenic mobilization processes. Many sources of mercury discharges to the environment have been documented. Significant progress has been made in controlling massive releases of mercury and mercury compounds from industrial sources such as the chlor-alkali process industry. Recently, however, certain areas of Ontario which are relatively free from industrial and municipal pollution have been shown to contain fish which have unexpectedly high concentrations of methyl-mercury.

The apparent absence or minimal presence of natural and/or man-made sources of mercury contamination in these areas and the generally very low measured concentrations of mercury in surface waters have led to speculation about the origin of mercury in the aquatic food chain. Atmospheric transport of mercury from distant industrialized areas has been suggested as a potential contributor to surface deposition. One possibility might be that mercury so deposited accumulates in sediments of lakes and streams and subsequently is mobilized into the food chain by micro-organisms.

Long-range transport of mercury would involve both particulate matter and vapour-phase mercury in various chemical forms. None of these parameters has been measured extensively or intensively enough in Ontario to permit an estimate of the deposition flux of mercury to the surface in either urbanized or rural areas.

The purpose of the program described by the terms of reference which follow is to provide information to aid in determining whether the atmosphere is a significant medium for mobilization of mercury in Ontario.



Objectives:

The proposed work programme must meet the following objectives:

1. To determine the total deposition flux of elemental mercury and its compounds from the atmosphere to land and water surfaces in specified geographic areas of Ontario. The program must provide a field determination of total wet and dry deposition of particulate and vapour mercury in its various chemical forms.
2. To develop and test field sampling methodology for mercury in precipitation (rain and snow) covering both composite and event collections;
3. To develop and test field sampling and analytical methodology for particulate and vapour mercury in air samples.
4. To determine the compounds of mercury which are present in airborne particulate matter collected on filter media, including size fractionated samples, and in vapour-phase samples;
5. To determine whether "high-volume" particulate sampling is representative of or correlated to atmospheric mercury concentrations, and to compare "high volume" results with those of other sampling techniques.
6. To carry out a field survey for mercury and its compounds in the atmosphere of geographic locations to be specified by the Ministry of the Environment.

Guidelines:

The proposed work programme will start with a literature and state-of-the-art review on relevant air pollution aspects of mercury. The work to accomplish the stated objectives is to be carried out in two stages. The first stage will begin with the development and verification of field sampling methodology for both precipitation and air samples (Items 2 and 3). Proven analytical methods for precipitation samples which are reliable and of the required sensitivity are already developed in the MOE Laboratory Services Branch and will be recommended, so that new analytical method develop-

ment for precipitation samples is not anticipated. However, the Laboratory Services Branch does not have adequate analytical sensitivity for particulate and vapour mercury in air samples, and analytical method development for air samples will be required (Item 3). The first stage will conclude with the set-up and operation of one field station (probably in the vicinity of either Toronto or Huntsville) at which monthly composite wet deposition samples and atmospheric aerosol samples will be collected for analysis for a period of about six months. The results of this preliminary sampling program will be evaluated jointly by the contractor and the Ministry staff to determine whether there is a need to carry out a more extensive survey.

Stage two will be optional depending on the conclusions reached at the end of the first stage. The second stage will comprise the operation of four sampling stations for precipitation and aerosol collection for a period of about twelve months. Area surveys across selected geographical transects in the vicinity of these stations may also be included. The techniques will be those which were verified in the first stage. The locations of these stations will be specified by the Ministry and will probably be located in the following areas; Toronto, Simcoe/Muskoka region, Haliburton region, Kawartha region.

Where feasible, composite precipitation sampling is to be augmented by event sampling in both stages.

An optional third stage would be to determine the relationship between proximity to major known sources of mercury emissions and the vapour/particulate fractionation of mercury and its compounds.

S. Gewurtz  
Air Resources Branch  
Ontario Ministry  
of Environment,  
September, 1977

TD  
887  
M37  
M47  
1978